

**METALLURGY AND CORROSION  
CONTROL IN OIL AND GAS  
PRODUCTION**



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# **METALLURGY AND CORROSION CONTROL IN OIL AND GAS PRODUCTION**

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**ROBERT HEIDERSBACH**



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*To Krista Heidersbach, my favorite corrosion engineer*

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# PREFACE

“Were I to wait perfection, my book would never be finished.” This quote from Tai K’ung in the thirteenth century is part of the preface to B. F. Brown’s book on stress corrosion cracking. I must quit writing sometime, and that time has come.

This Preface is my opportunity to let readers know what I have attempted to do with this book. In my many years of consulting, teaching, and research, I have been exposed to the oil and gas industry in many countries. The problems are similar, and this book is an attempt to address the most important issues. I have not tried to cover everything important on any given subject; entire books have been written about each of the major subjects. Instead, in this book, I have tried to condense into a concise format:

- Basic principles
- Standards and references for further reading

There are other books on this general subject, and my reason for writing this one is to consolidate into one volume useful information on metallurgy and on the various means of corrosion control.

My own training as a metallurgical engineer prepared me to deal with exotic alloys, but my first two projects in industry after my graduation were on corrosion in concrete and on cathodic protection. From this experience I learned several points that have guided my career and that I have tried to emphasize in this book:

- Most formal education will not cover the specifics useful to a professional’s career.
- Most metals used by industry are carbon and low-alloy steels. This means that protective coatings,

chemical treatment using inhibitors and scavengers, and cathodic protection are every bit as important as metallurgy.

There is a saying that goes something like this: “If you want to learn a subject, teach it.” Most of the subjects covered in this book have been suggested by participants in classes I have taught worldwide to industrial audiences. During my career as a professor, I tried to bring into the classroom the lessons taught to me from these industrial courses and from my consulting practice.

Compared with other books on similar subjects, this book has many illustrations, including photographs of problems encountered in the field. It is my hope that these pictures will be useful aids to understanding the subjects under discussion. Many of the illustrations, and the subjects they address, have been suggested by participants in my classes. I always learn more from the classes than I am able to teach. I thank each and every participant for his/her input into how this book was developed.

I have learned over the years that many formally educated corrosion professionals are either engineers or chemists by training. While these two groups represent the largest two categories of backgrounds in the oilfield corrosion control industry, they are in the minority. Those having many other educational backgrounds are also involved in oilfield corrosion control. Most engineers, with the exception of chemical engineers, have little formal education in chemistry, and what chemistry they learned did not emphasize corrosion-related subjects. This is understandable, because most chemistry classes have students from a variety of interests—engineering, agriculture, pharmacy, and so on. It is impossible to emphasize what is important to each field in

courses taught to such diversified audiences. Chemists seldom have training in fluid flow, heat transfer, metallurgy, and a variety of other subjects standard to most engineering curricula and important to oilfield problems. I have provided brief chapters emphasizing the corrosion and maintenance aspects of both chemistry and materials. These chapters are intended to be useful for someone needing a refresher to help understand the chapters that follow. Ideas related to corrosion, many of which are not covered in university courses, are also discussed.

The latter chapters of the book are intended to explain field problems and give some insight into how many organizations have addressed these problems. I hope the reader will find them useful.

It is now my opportunity to thank those organizations and people who have helped the most in the preparation of this book.

I have been fortunate to have conducted research or taught classes for all of the “super-major” oil companies and for other companies in a variety of countries. Participation in these classes has taught me what is important to operating company employees, both corrosion professionals and other engineers and technicians who must address corrosion as part of their broader responsibilities.

People who have helped with this book include Charlie Speed, from the NACE New Orleans section, who donated files from industrial courses he has taught on this subject. Jack Smart gave the best talk on corrosion, inspection, and wave loading I have ever heard at the NACE convention in Chicago. This presentation was made the same month as the Alexander Kielland disaster in the North Sea. There is no telling how many lives Jack’s efforts on offshore platform corrosion assessment

have saved. Some of Jack’s publications are referenced in this book. Mark Rackley, a pipeliner and an excellent communicator, taught me much about both internal and external corrosion problems. He also did it in an entertaining manner, and that helped to keep the lessons fresh in his audience’s memories. Richard Norsworthy is my other pipeline expert and a much-appreciated colleague. His public questioning of attempts to make cathodic protection unnecessarily complicated are invaluable. When I need coatings advice, I call on Jerry Byrd, and he always helps. Jerry Bauman works for a design firm and taught me the importance of Pitting Resistance Equivalent Numbers (PRENs) for alloys. I also rely on him for other oilfield metallurgy advice. Many oil companies have excellent metallurgy and corrosion groups. When I was at Oklahoma State University, I was fortunate enough to meet and learn from the people at what has become ConocoPhillips. Mike Joosten, Juri Kolts, Jay Murali, Mamdouh Salama, and Bill Thomason have all taught me important lessons that are reflected in this book.

Most of the people mentioned above had training as engineers or chemists. Their contributions to this book have been important. The hundreds of technicians, most of whom I cannot identify, who taught me what really happens in the field, have made even greater contributions to this book. I thank them all.

This book would have never been written without the support and encouragement of Dianne Heidersbach, my wife of 47 years. I thank her most of all.

BOB HEIDERSBACH

*Cape Canaveral, Florida  
May 2010*

## INTRODUCTION TO OILFIELD METALLURGY AND CORROSION CONTROL

The American Petroleum Institute (API) divides the petroleum industry into the following categories:

- Upstream
- Downstream
- Pipelines

Other organizations use terms like production, pipelining, transportation, and refining. This book will discuss upstream operations, with an emphasis on production, and pipelines, which are closely tied to upstream operations. Many “pipelines” could also be termed gathering lines or flowlines, and the technologies involved in materials selection and corrosion control are similar for all three categories of equipment.

Until the 1980s, metals used in upstream production operations were primarily carbon steels. Developments of deep, hot gas wells in the 1980s led to the use of corrosion-resistant alloys (CRAs), and this trend continues as the industry becomes involved in deeper and more aggressive environments.<sup>1</sup> Nonetheless, the most used metal in oil and gas production is carbon steel or low-alloy steel, and nonmetallic materials are used much less than metals.

Increased emphasis on reliability also contributes to the use of newer or more corrosion-resistant materials. Many oil fields that were designed with anticipated operating lives of 20–30 years are still economically viable after more than 50 years. This life extension of oil fields is the result of increases in the market value of

petroleum products and the development of enhanced recovery techniques that make possible the recovery of larger fractions of the hydrocarbons in downhole formations. Unfortunately, this tendency to prolong the life of oil fields creates corrosion and reliability problems in older oil fields when reductions in production and return on investment cause management to become reluctant to spend additional resources on maintenance and inspection.

These trends have all led to an industry that tends to design for much longer production lives and tries to use more reliable designs and materials. The previous tendency to rely on maintenance is being replaced by the trend to design more robust and reliable systems instead of relying on inspection and maintenance. The reduction in available trained labor for maintenance also drives this trend.

### COSTS

A U.S. government report estimated that the cost of corrosion in upstream operations and pipelines was \$1372 billion per year, with the largest expenses associated with pipelines followed by downhole tubing and increased capital expenditures (CRAs, etc.). The most important opportunity for savings is the prevention of failures that lead to lost production. The same report suggested that the lack of corrosion problems in existing systems does not justify reduced maintenance budgets, which is a recognition that as oil fields age, they become more corrosive at times when reduced returns on investment are occurring.<sup>2</sup> It is estimated that corrosion costs are approximately equal to mechanical breakdowns in maintenance costs.



**Figure 1.1** Natural gas pipeline rupture near Carlsbad, New Mexico, in 2000.<sup>3</sup>

## SAFETY

While proper equipment design, materials selection, and corrosion control can result in monetary savings, a perhaps more important reason for corrosion control is safety. Hydrogen sulfide,  $H_2S$ , is a common component of many produced fluids. It is poisonous to humans, and it also causes a variety of environmental cracking problems. The proper selection of  $H_2S$ -resistant materials is a subject of continuing efforts, and new industrial standards related to defining metals and other materials that can safely be used in  $H_2S$ -containing (often called “sour”) environments are being developed and revised due to research and field investigations.

Pipelines and other oilfield equipment frequently operate at high fluid pressures. Crude oil pipelines can leak and cause environmental damage, but natural gas pipeline leaks, like the corrosion-related rupture in Carlsbad, New Mexico, shown in Figure 1.1, can lead to explosions and are sometimes fatal.<sup>3</sup> High-pressure gas releases can also cause expansive cooling leading to brittle behavior on otherwise ductile pipelines. API standards for line pipe were revised in 2000 to recognize this possibility. Older pipelines, constructed before the implementation of these revised standards, are usually made from steel with no controls on low-temperature brittle behavior and may develop brittle problems if they leak. Gas pipelines are more dangerous than liquid pipelines.



**Figure 1.2** Above-ground leak from an internally corroded crude oil pipeline.



**Figure 1.3** An oil containment boom to minimize the spread of crude oil from a corroded pipeline.

## ENVIRONMENTAL DAMAGE

Environmental concerns are also a reason for corrosion control. Figure 1.2 shows oil leaking from a pipeline that suffered internal corrosion followed by subsequent splitting along a longitudinal weld seam. The damages due to this leak are minimal compared with the environmental damages that would have resulted if the leak had been on a submerged pipeline. Figure 1.3 shows an oil containment boom on a river where a submerged crude oil pipeline was leaking due to external corrosion caused by non-adherent protective coatings that shielded the exposed metal surfaces from protective cathodic protection currents.



## CORROSION CONTROL

The environmental factors that influence corrosion are:<sup>4</sup>

- CO<sub>2</sub> partial pressure
- H<sub>2</sub>S partial pressure
- Fluid temperature
- Water salinity
- Water cut
- Fluid dynamics
- pH

Corrosion is normally controlled by one or more of the following:

- Material choice
- Protective coatings
- Cathodic protection
- Inhibition
- Treatment of environment
- Structural design including corrosion allowances
- Scheduled maintenance and inspection

Figure 1.4 shows an offshore platform leg in relatively shallow water, approximately 30m (100ft) deep, in Cook Inlet, Alaska. The leg is made from carbon steel, which would corrode in this service. Corrosion control is provided by an impressed current cathodic protection system. The bottom of the leg is 2.5cm (1in.) thicker than the rest of the leg, and this is intended as a corrosion allowance for the submerged portions of the platform legs. Note that the water level goes above the corrosion allowance twice a day during high tides, because the platform is located in water 3m (10ft) deeper than was intended during design and construction. Fortunately, the cathodic protection system was able to provide enough current, even in the fast-flowing abrasive tidal waters of Cook Inlet, to control corrosion. This platform was obsolete when the picture was taken, but it was less expensive to operate and maintain the platform than it was to remove it. Thirty-five years



**Figure 1.4** Offshore platform leg in Cook Inlet, Alaska. The extra metal for the corrosion allowance is submerged twice a day during high tides.

later, oil prices had increased, recovery methods had improved, and the platform was economically profitable. Robust designs, adequate safety margins, and continuous re-evaluation of corrosion control methods are important, not just for marine structures, but for all oilfield equipment.

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## CHEMISTRY OF CORROSION

Corrosion, the degradation of a material due to reaction(s) with the environment, is usually, but not always, electrochemical in nature. For this reason, an understanding of basic electrochemistry is necessary to the understanding of corrosion. More detailed descriptions of all phenomena discussed in this chapter are available in many general corrosion textbooks.<sup>1-8</sup>

### ELECTROCHEMISTRY OF CORROSION

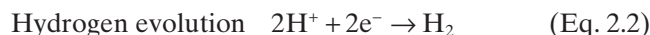
Most corrosion involves the oxidation of a metal which is accompanied by equivalent reduction reactions which consume the electrons associated with the corrosion reaction. The overall corrosion reactions are often referred to separately as “half-cell” reactions, but both oxidation and reduction are interrelated, and the electrical current of both anodes, where oxidation is prevalent, and cathodes, where reduction predominates, must be equal in order to conserve electrical charges in the overall system.

#### Electrochemical Reactions

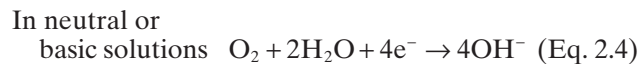
A typical oxidation reaction for carbon steel would be:



Common reduction reactions associated with corrosion include:



Oxygen reduction



Metal ion reduction or deposition is also possible:



The reduction reaction is usually corrosion-rate controlling because of the low concentrations of the reducible species in most environments compared with the high concentration (essentially 100%) of the metal. As one example, the dissolved oxygen concentration in most air-exposed surface waters is slightly lower than 10 ppm (parts per million). This relatively low dissolved oxygen concentration is usually much higher than the concentration of any other reducible species, and the control of air leakage into surface facilities is a primary means of controlling internal corrosion in topside equipment and piping.

More than one oxidation or reduction reaction may be occurring on a metal surface, for example, if an alloy is corroding or if an aerated acid has high levels of dissolved oxygen in addition to the hydrogen ions of the acid.

Electrochemical reactions occur at anodes, locations of net oxidation reactions, and at cathodes, locations of net reduction reactions. These anodes and cathodes can

be very close, for example different metallurgical phases on a metal surface, or they can have wide separations, for example, in electrochemical cells caused by differences in environment or galvanic cells between anodes and cathodes made of different materials.

### Electrolyte Conductivity

The electrical conductivity of an environment is determined by the concentration of ions in the environment, and the resulting changes in corrosivity can be understood by considering Ohm's Law:

$$E = IR \quad (\text{Eq. 2.7})$$

where:

E = the potential difference between anode and cathode, measured in volts

I = the electrical current, measured in amperes

R = the resistance of the electrical circuit, determined by the distances between anode and cathode and by  $\rho$ , the resistivity of the electrolyte, which is usually expressed in ohm-centimeters ( $\Omega\text{-cm}$ ). In most cases, the distance between anode and cathode is not known, but the changes in the corrosion rate can be monitored and correlated in changes in resistivity, for example, the changes in resistivity of soils caused by changes in moisture content which alter the ionic content of the soil electrolyte.

The resistivity of liquids and solids is determined by the ions dissolved in the bulk solution. Hydrocarbons such as crude oil, natural gas, and natural gas condensates are covalent in nature and are very poor electrolytes because they have very high resistivities. Oilfield corrosion is usually caused by chemicals in the water phase that, among other things, lower the natural resistivity of water, which is also mostly covalent. Water is a very efficient solvent for many chemicals, and most oilfield corrosion occurs when metal surfaces become wetted by continuous water phases having dissolved chemicals which lower the natural high resistivity (low conductivity) of water.

### Faraday's Law of Electrolysis

The mass of metal lost due to anodic corrosion currents can be determined from Faraday's law for electrolysis, Equation 2.8, which is also used by the electroplating industry:

$$W_{\text{corroded}} = \frac{F(i)tM}{n} \quad (\text{Eq. 2.8})$$

where:

$W_{\text{corroded}}$  = mass (weight) of corroded/electrodeposited metal

F = Faraday's constant

i = current in amps

t = time of current passage

m = molar mass of the element in question

n = ionic charge of the metal in question

The amount of a substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell. Methods of measuring the corrosion current are difficult and are discussed in Chapter 7, Inspection, Monitoring, and Testing.

### Electrode Potentials and Current

The Electromotive Force (EMF) Series is an orderly arrangement of the relative standard potentials for pure metals in standard, unit activity (1 Normal, 1N), solutions of their own ions (Table 2.1). The more active metals on this list tend to be corrosion susceptible and the less active, or noble metals, will resist corrosion in many environments.

It should be noted that two sign conventions are followed in publishing the EMF series. This can cause confusion, which can be avoided if the reader understands that active metals like magnesium and aluminum will always be anodic to carbon steel, and corrosion-resistant metals like silver and palladium will be cathodic.

The EMF series shows equilibrium potentials for pure metals in 1N (one normal or unit activity of ions) solutions of their own ions. While this is the basis for much theoretical work in corrosion and other areas of electrochemistry, pure metals are seldom used in industry, and oilfield corrosive environments never have 1N metal ion concentrations. The more practical galvanic series (Figure 2.1), which shows the relative corrosion potentials of many practical metals, is often used in corrosion control. This is based on experimental work in seawater and serves as the basis for many corrosion-related designs.

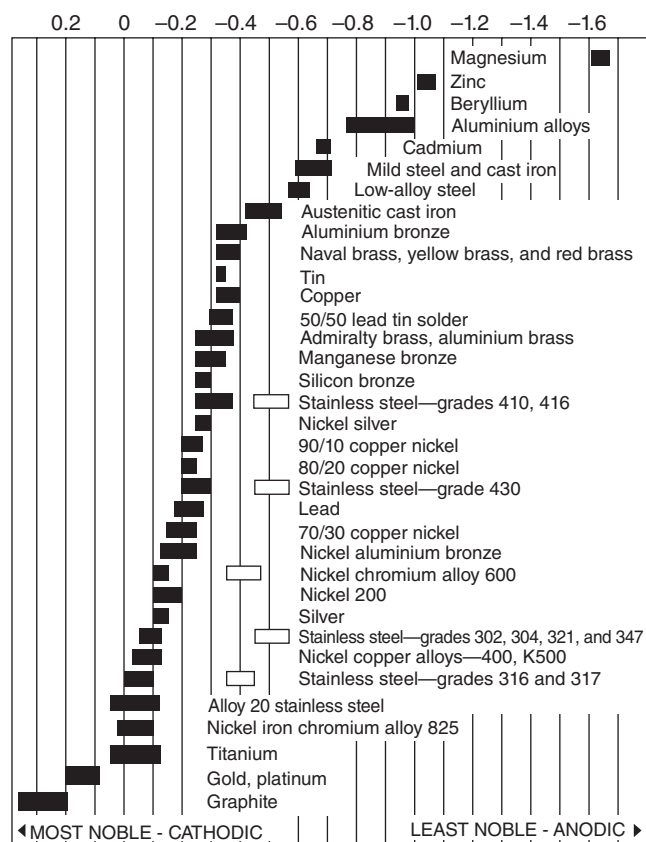
The galvanic series in seawater shown in Figure 2.1 is widely used for engineering designs. Some authorities claim that the relationships between various alloys must be determined for each environment, but this is seldom done. The reason for this precaution is that zinc and



**TABLE 2.1 The Electromotive Force Series for Selected Metals**

	Metal	Ion Formed	Potential	
Anodic	Magnesium	$Mg^{+2}$	+2.96	Active
	Aluminum	$Al^{+3}$	+1.70	
	Zinc	$Zn^{+2}$	+0.76	
	Iron	$Fe^{+2}$	+0.44	
	Nickel	$Ni^{+2}$	+0.23	
	Tin	$Sn^{+2}$	+0.14	
	Lead	$Pb^{+2}$	+0.12	
	Hydrogen	$H^{+1}$	0.00	
	Copper	$Cu^{+2}$	-0.34	
	Silver	$Ag^{+1}$	-0.80	
Cathodic	Palladium	$Pd^{+2}$	-0.82	Noble

Source: Adapted from M. Parker and E. Peattie, *Pipeline Corrosion and Cathodic Protection*, 3rd ed. (Gulf Publishing, Houston, TX, 1984; 1995 reprinting), p. 157.

**Figure 2.1** Galvanic series in seawater.

carbon steel undergo a polarity reversal in some freshwaters at approximately 60°C (140°F). The only other polarity reversal that has been reported is when tin, which would normally be cathodic to carbon steel, becomes anodic to carbon steel in deaerated organic acids, such as are found in the common tin cans used

for food storage. It is unlikely that any other polarity reversals will be found in oilfield environments, and designers should assume that the relationships shown in Figure 2.1 are valid. Revie and Uhlig offer a brief review of polarity reversals.<sup>2</sup>

The Nernst equation, first published in 1888 by the German chemist who later won the 1920 Nobel Prize in chemistry, explains how potentials of both anodic and cathodic reactions can be influenced by changes in the temperature and chemical compositions of the environment. The reduction potential can be expressed as:

$$\text{Nernst equation} \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]} \quad (\text{Eq. 2.9})$$

where:

$E$  = the electrochemical potential of the reaction in question

$E^\circ$  = the standard electrode potential at 25°C in a 1 N solution of the ion formed by oxidation of the reactants in question

$R$  = the universal gas constant = 8.31 Joules/gram mole K

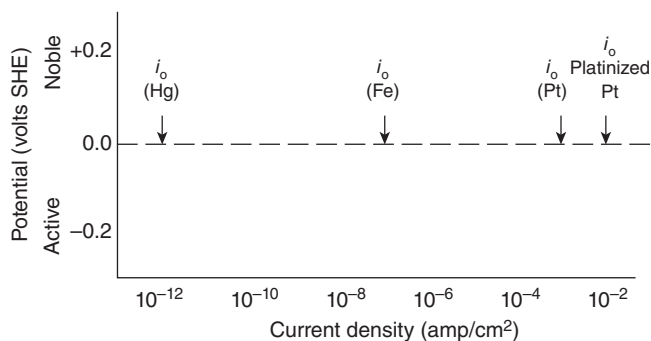
$T$  = the absolute temperature, Kelvin

$n$  = the charge on the ion being reduced

$F$  = Faraday's constant = 96,500 coulombs/gram-equivalent

At standard temperature conditions, this equation can be simplified to:

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$



**Figure 2.2** Hydrogen-hydrogenion exchange current densities.

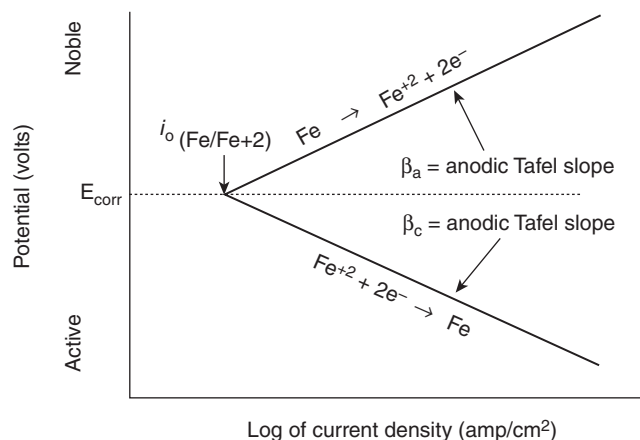
The details of this relationship are described in many general corrosion textbooks.<sup>1-7</sup> What is important to understand for oilfield corrosion control is that electrochemical cells (corrosion cells) can be caused by changes in:

- Temperature
- Chemical concentrations in the environment

Both types of electrochemical cells are important in oilfield corrosion and will be discussed further in Chapter 5, Forms of Corrosion.

It is simplistic to describe a chemical reaction as either oxidation or reduction. In actuality, the reversible chemical reactions are happening in both directions simultaneously. The equilibrium potential, determined by the Nernst equation, is the potential where the oxidation and reduction currents, measured in current density on an electrode surface, are equal. The current density at this point is called the exchange current density. Some metals, for example, the platinum and palladium used in impressed current anodes, have very high exchange current densities. This means that a small surface area of these materials can support much higher anodic currents than other anode materials such as high-silicon cast iron or graphite. Figure 2.2 shows exchange current densities for hydrogen oxidation/reduction reactions. A platinum surface can support 10,000 times the current density of an iron anode for the same reaction. This increase in efficiency is used in the cathodic protection industry to justify the use of relatively expensive precious metal surfaces to replace much heavier, and therefore harder to install, high-silicon cast iron anodes.

As potentials change from the equilibrium potential, the electrode surface becomes either an anode or a cathode. It is common to plot the shifts in potential on linear-logarithmic plots because in many cases, these plots produce a region of activation-controlled elec-



**Figure 2.3** Activation polarization of an iron electrode.

trode behavior where the voltage of anodes and cathodes follows a log-linear pattern, called the Tafel slope, after the German scientist who first explained this behavior in 1905.

On an anode, the Tafel equation can be stated as:

$$\eta_a = \beta_a \ln \left( \frac{i}{i_0} \right) \quad (\text{Eq. 2.10})$$

where:

$\eta_a$  = the overpotential, or change between the measured potential and the potential at the current density of interest. The subscript “a” indicates that this polarization is “activation polarization” which occurs at low current densities near the equilibrium potential.

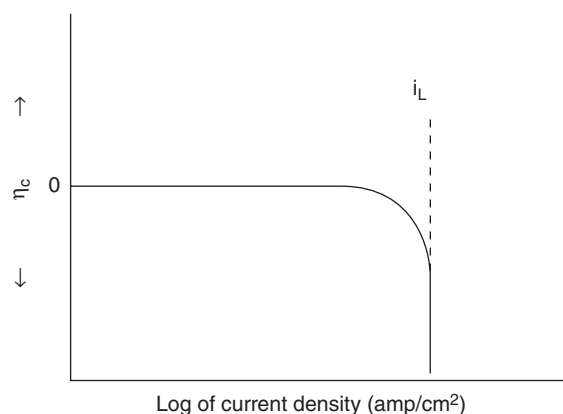
$\beta_a$  = the so-called “Tafel slope”

$i$  = the current density, A/m<sup>2</sup>

$i_0$  = the exchange current density, A/m<sup>2</sup>.

At low electrode current densities, the change in potential can be plotted as shown in Figure 2.3. These plots of potential versus logarithm of current are often termed Evans diagrams, after Professor U. R. Evans of Cambridge University, who popularized their use.<sup>5</sup>

As stated above, most oilfield corrosion rates are controlled by the low concentrations of reducible species in the environment. These species must migrate, or diffuse, to the metal surface in order to react. The rate of this diffusion is controlled by the concentration of the diffusing species in the environment, the thickness of the boundary layer where this diffusion is occurring (largely determined by fluid flow or the lack thereof), temperature, and other considerations. The resulting concentration polarization can be written as:



**Figure 2.4** Concentration polarization curve for a reduction reaction.

$$\eta_c = 2.3 \frac{RT}{nF} \log(1 - i/i_L) \quad (\text{Eq. 2.11})$$

where:

$\eta_c$  = the overpotential, or polarization, caused by the diffusion of reducible species to the metal surface

$F$  = Faraday's constant

$i$  = the current on the electrode

$i_L$  = the limiting current density determined by the diffusivity of the reducible species; this is the maximum rate of reduction possible for a given corrosion system

The other terms are the same as described above in discussions of the Nernst equation and activation polarization (Tafel slope) behavior.

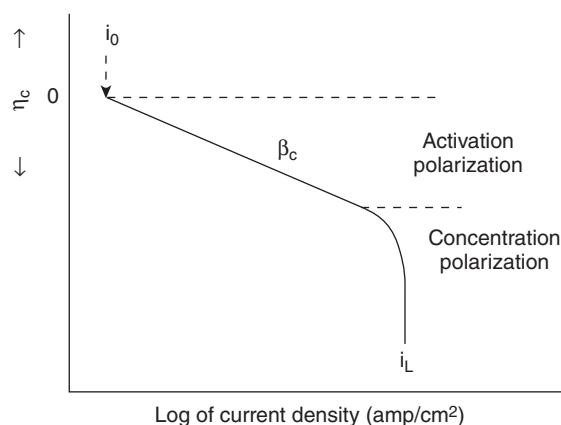
Concentration polarization is shown in Figure 2.4. In corrosion, the limited concentrations of reducible species produce concentration polarization only at cathodes. At low current densities, the concentration polarization is negligible, and, as the reduction current density approaches the limiting current, the slope quickly becomes a vertical downward line.

The total polarization of an electrode is the sum of both the activation and concentration polarization. The combined polarization for a reduction reaction on a cathode is:

$$\eta_{\text{red}} = -\beta_c \log i/i_0 + 2.3 \frac{RT}{nF} \log(1 - i/i_L) \quad (\text{Eq. 2.12})$$

This is shown in Figure 2.5.

As stated earlier, most oilfield corrosion rates are determined by the concentration of the reducible chemicals in the environment. Figure 2.6a shows how the



**Figure 2.5** Combined polarization curve for activation and concentration polarization on a cathode.

polarization of both the oxidation of a metal and the reduction of hydrogen ions determines the corrosion rate,  $i_{\text{corr}}$ , and the corrosion potential,  $E_{\text{corr}}$  for a generic metal.

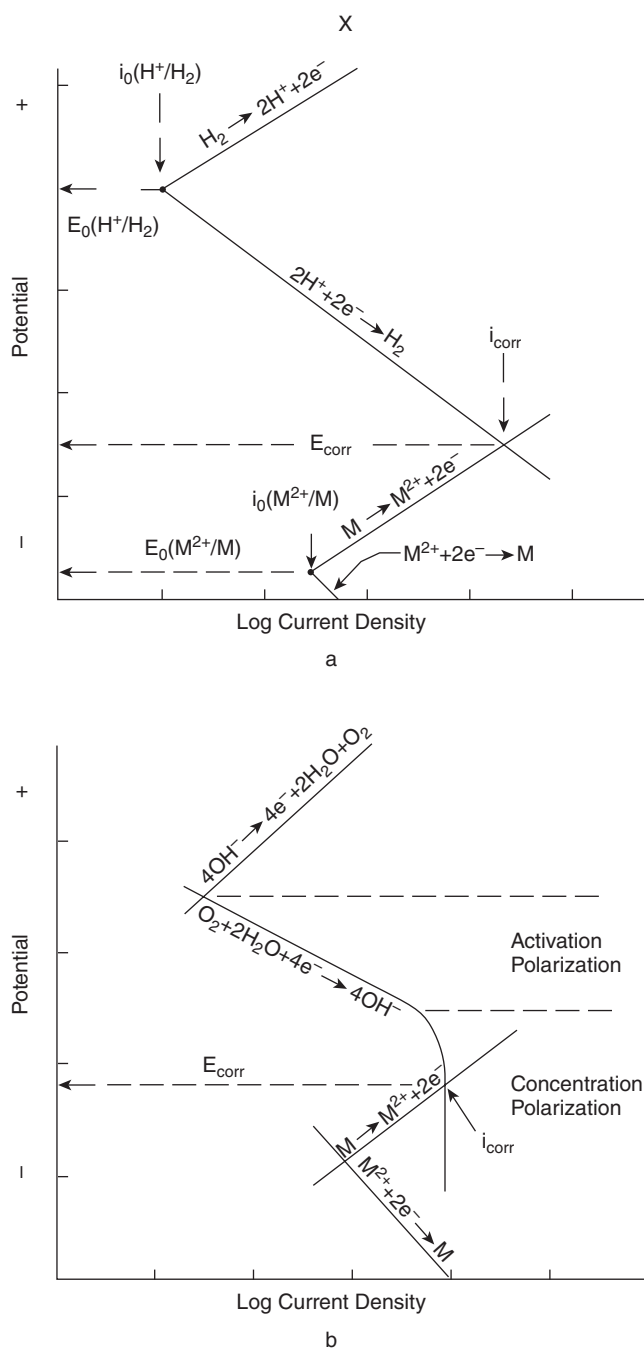
For surface equipment, most corrosion rates are determined by the concentration of dissolved oxygen in whatever water is available. This is shown in Figure 2.6b, where the oxidation line showing Tafel behavior intersects the vertical (concentration limited) portion of the reduction reaction.

The importance of potential in determining corrosion rates is apparent from the above discussions. Academic chemistry reports tend to describe potentials relative to the standard hydrogen electrode, which has been arbitrarily set to a potential of zero. In field applications, it is common to use other reference electrodes. The most common reference electrodes used in oilfield work are the saturated copper-copper sulfate electrode (CSE), used in onshore applications, and the silver-silver chloride electrode used for offshore measurements, where contamination of the CSE electrode would produce variable readings. Table 2.2 shows conversion factors for these electrodes and other commonly used reference electrodes compared with the standard hydrogen electrode (SHE). As an example, an electrode which measures  $-0.300\text{V}$  versus CSE would measure  $+0.018\text{V}$  versus SHE. Figure 2.7 shows a standard copper-copper sulfate electrode.

## CORROSION RATE EXPRESSIONS

Corrosion rates are measured in a number of ways:

- Depth of penetration
- Weight loss



**Figure 2.6** (a) Corrosion current and potential of iron determined by the polarization of iron and the hydrogen reduction reaction.<sup>9</sup> (b) Corrosion current and potential of iron determined by the concentration polarization of oxygen.<sup>9</sup>

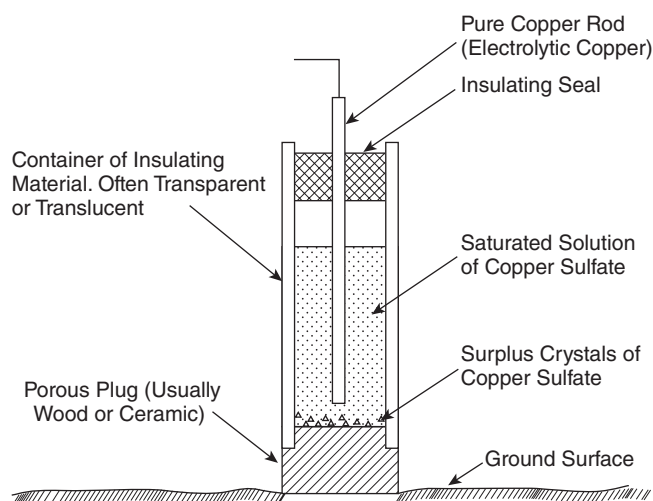
- Electrical current associated with corrosion
- Time to failure

The simplest of these concepts to understand is depth of penetration. It can be expressed in mm/yr (millime-

**TABLE 2.2** Potential Values for Common Reference Electrodes

Name	Potential V vs. SHE
Copper-copper sulfate	+0.318
Saturated calomel	+0.241
Silver-silver chloride	+0.222
Standard hydrogen	+0.000

Adapted from Reference 3.



**Figure 2.7** Saturated copper-copper sulfate reference electrode.<sup>9</sup>

ters per year) or mpy (mils or thousandths of an inch per year). The loss of wall thickness is often used to determine remaining equipment life or safe operating pressures for piping systems, storage tanks, and so on. Table 2.3 shows a commonly used classification of relative corrosion rates. The U.S. Standard units, mpy, produce small numbers that are easy to understand, and corrosion rates in mpy are commonly used worldwide, although other expressions are also common.<sup>1</sup>

Weight loss measurements are commonly used on exposure samples used to monitor corrosion rates in oil and gas production. It is a simple matter to convert these weight loss measurements into average depths of penetration, although this can be very misleading, because most corrosion is localized in nature and the average penetration rate seldom gives an indication of the true condition of oilfield equipment.

The electrical current associated with anodic dissolution of a metal can be used to determine the corrosion rate using Faraday's law. This calculation of mass loss

**TABLE 2.3 Relative Corrosion Resistance versus Annual Penetration Rates**

Relative Corrosion Resistance	Corrosion Rate	
	mpy	mm/yr
Outstanding	<1	<0.02
Excellent	1–5	0.02–0.1
Good	5–20	0.1–0.5
Fair	20–50	0.5–1
Poor	50–200	1–5
Unacceptable	200+	5+

Source: Adapted from M. Fontana, *Corrosion Engineering* (McGraw-Hill, 1986).<sup>1</sup>

can be converted into remaining thickness. Once again, the reader is cautioned that most corrosion is localized in nature and calculations assuming uniform loss of cross section are frequently misleading.

The time to failure, however defined, is the most common concern of managers and operators of equipment. For some forms of corrosion testing, for example, stress corrosion cracking, the time to failure is used to screen alloys, environments, or other variables.

## pH

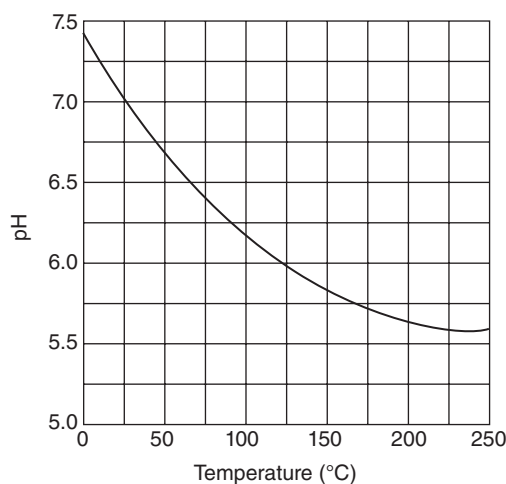
The pH of an environment is one of the major factors determining if corrosion will occur. It also influences the type of corrosion that is experienced.

pH is defined as:

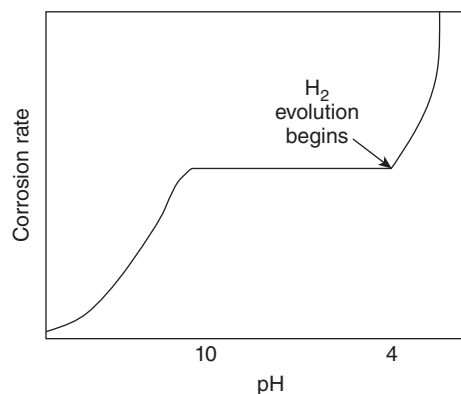
$$\text{pH} = -\log[\text{H}^+] \quad (\text{Eq. 2.13})$$

where the  $[\text{H}^+]$  expression shows the hydrogen ion activity of the environment.

The  $[\text{H}^+]$  depends on the ionization of water and varies with temperature. The pH of neutral water at standard temperature (25°) is 7.00, but neutrality varies with temperature as shown in Figure 2.8. Downhole oilfield temperatures are usually elevated, and it is common to calculate the *in situ* pH of any fluids that might affect corrosion or scale deposition. There are many software packages available for this purpose. Figure 2.9 shows the effects of pH on the corrosion rates of iron in water. At low pHs, bare metal is exposed to the environment, and acid reduction on the surface controls corrosion rates. For intermediate pHs, a partially protective film of iron oxide reduces the corrosion rate and the diffusion of oxygen to cathodic locations on the metal surface controls. As the pH increases to even higher values, the surface becomes covered with mineral scales and corrosion is reduced.



**Figure 2.8** pH values of pure water at various temperatures.<sup>10</sup>



**Figure 2.9** The effect of pH on the corrosion rate of iron in water at room temperature. Adapted from W. R. Revie and H. H. Uhlig, *Corrosion and Corrosion Control*, Wiley-Interscience, 2008.

## PASSIVITY

Passivity is a phenomenon that is frequently misunderstood. Most metals form oxide films in most corrosive environments. These passive films can be protective and retard or even effectively stop corrosion, but they can also lead to fairly deep localized corrosion in situations where the protective films are removed or defective. Except in rare circumstances, the oxide films formed on carbon steel are not adequately protective, and other means of corrosion control are necessary. This is in contrast to stainless steels, titanium, and aluminum—oilfield metals that form protective passive films which are commonly the primary means of corrosion control for these alloys. On many corrosion-resistant alloys

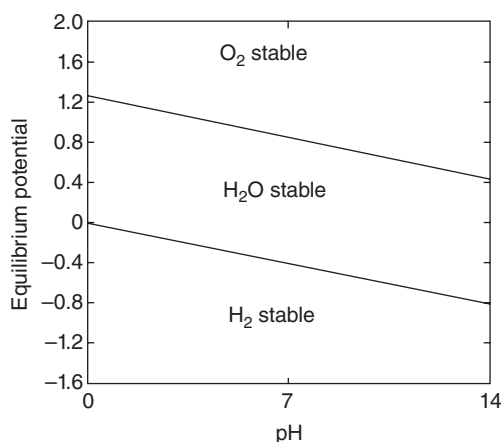


Figure 2.10 Potential-pH (Pourbaix) diagram for water.<sup>14</sup>

such as stainless steels, the passive films may be only dozens of atoms thick. This means that they are very weak and are subject to mechanical damage, and this can lead to localized corrosion at the damaged locations.

### Potential-pH (Pourbaix) Diagrams

Marcel Pourbaix developed a means of explaining the thermodynamics of corrosion systems by plotting regions of thermodynamic stability of metals and their reaction plots on potential versus pH plots.<sup>10-12</sup> The regions of a Pourbaix diagram can be described as:

- **Immunity** The metal cannot oxidize or corrode (although it may still be subject to hydrogen embrittlement).
- **Corrosion** Ions of the metal are thermodynamically stable and the metal will corrode.
- **Passivity** Compounds of the metal and chemicals from the environment are thermodynamically stable, and the metal may be protected from corrosion if the passive film is adherent and protective.

Many users of Pourbaix diagrams miss the final point above. Thermodynamics alone cannot predict if passive films will be protective or not.<sup>2,11-14</sup>

Figure 2.10 shows the Pourbaix diagram for water. Water is thermodynamically stable over a potential region of 1.23V, and the potentials at which oxidation and evolution (bubbling off) of oxygen from water at the top of the diagram or the evolution of hydrogen at the bottom of the diagram depend on the pH of the environment.

The Pourbaix diagram of iron is superimposed on the diagram for water in Figure 2.11. Similar diagrams are

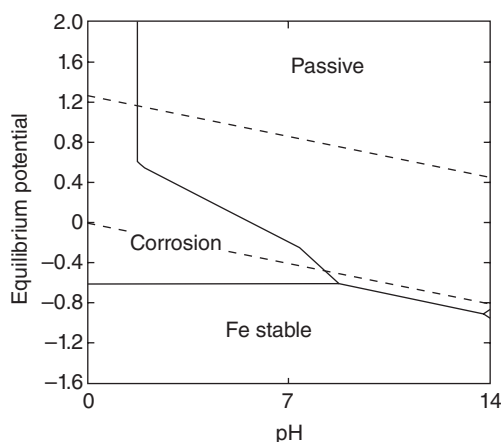


Figure 2.11 Potential-pH (Pourbaix) diagram for iron.<sup>14</sup>

available for most structural metals for which thermodynamic data are available (Figure 2.11).<sup>2,11-14</sup>

These diagrams make a number of important points useful for oilfield corrosion control:

- Water is only stable over a potential range of slightly more than one volt. This is very important in cathodic protection.
- Iron (carbon steel) is covered with iron oxides (passive films) in most aqueous environments. Unfortunately, these passive films are usually not sufficiently protective and other means of corrosion control are necessary.
- The potentials at which iron (carbon steel) is protected from corrosion do not coincide with the immunity regions on the Pourbaix diagram. This point is discussed in greater detail in Chapter 6, Corrosion Control.

The diagrams for zinc, aluminum, and cadmium, commonly referred to as the amphoteric coating metals, have passive regions in neutral environments. These metals also have low corrosion rates in neutral environments and higher corrosion rates in both acids and bases.

Pourbaix diagrams have limitations in addition to the inability of thermodynamics to predict the protectiveness of passive films. These include the idea that they can only be calculated for alloys, although experimental Pourbaix diagrams have been reported.<sup>12,13</sup> Revie and Uhlig list other limitations.<sup>2</sup>

### SUMMARY

The following ideas have been discussed in detail in this chapter:



- Corrosion is electrochemical in nature.
- Most metal surfaces have both oxidation and reduction occurring simultaneously.
- If the predominant reaction is oxidation, the metal will corrode.
- The most important reduction reaction is oxygen reduction for many oilfield systems. If no oxygen is available, the corrosion rate will often be very low.

Electrode potentials are determined by:

- Metal chemistry
- Chemicals in the environment
- Temperature

These potentials are usually measured against either copper-copper sulfate or silver-silver chloride electrodes, depending on the environment.

Corrosion rates are often expressed by average depth of penetration, and this can be misleading because most oilfield corrosion is localized in nature.

The pH of the environment has a major effect on corrosivity.

Passive films may limit corrosion in many environments, but carbon steel, the most common oilfield metal, seldom forms adequately protective passive films, and other means of corrosion are often necessary.

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## CORROSIVE ENVIRONMENTS

A very limited amount of oilfield corrosion is associated with very high temperature atmospheric exposures, common in flares, and with liquid metals, usually mercury found in natural gas and some crude oils. The great majority of oilfield corrosion requires liquid water. For this reason, as an oil field ages and the water cut increases, corrosion also increases. This is shown in Figure 3.1, which shows the effect of water cut on corrosion rates.<sup>1</sup> Many operators use rules of thumb such as the idea that corrosion is not a problem until the water cut reaches 40% or 50%. For some oil fields, this may take several years before corrosion becomes a problem. Unfortunately, this means that corrosion and other maintenance problems become more important at a time when maintenance funds, often related to production rates, decrease.

Water has very limited solubility in hydrocarbons, and the presence of a separated water phase is necessary for corrosion. The low-corrosion region in Figure 3.1 is where most of the metal surface is in contact with a water-in-oil emulsion. The small water droplets are not continuous, and most of the metal surface is in contact with nonconductive hydrocarbons. As the water cut increases, the amount of the metal surface in contact with water gradually increases until the emulsion reverses, and the liquid becomes continuous water with entrained hydrocarbon droplets. Production and fluid flow rates, along with temperature and pressure considerations, determine when this will happen. Figure 3.2 shows how water separates out on production tubing.

In contrast to oil wells, natural gas wells are corrosive from the beginning. This is due to the fact that all natural gas reservoirs will produce some water, and minor components of the natural gas, which condense from the gas stream as temperatures and pressures are reduced, dissolve in this water and make it corrosive.

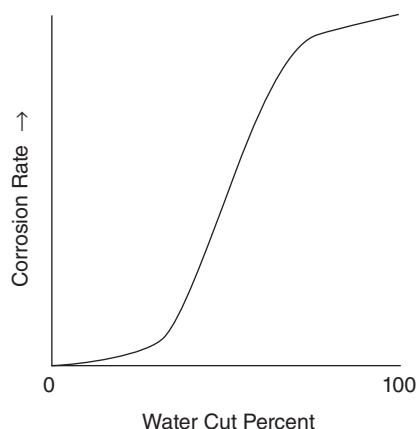
Most downhole hydrocarbon reservoirs have virtually no dissolved oxygen in the fluids, and this is fortunate, because the presence of oxygen at the parts-per-billion (ppb) level has been shown to promote corrosion. This is in contrast to carbon dioxide ( $\text{CO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ), which may be present in varying quantities in both oil and gas fields. The relative effects of these three gases are shown in Figure 3.3. Oxygen is approximately 50 times more corrosive than  $\text{CO}_2$  and more than a hundred times more corrosive than  $\text{H}_2\text{S}$ .<sup>3</sup>

Downhole corrosion, in the absence of oxygen, is largely determined by the concentrations of  $\text{CO}_2$  or  $\text{H}_2\text{S}$  in the produced fluids. The terms “sweet corrosion” to describe corrosion caused by  $\text{CO}_2$ , and “sour corrosion” to describe problems with  $\text{H}_2\text{S}$ , have been used for many years to differentiate which of these two gases is likely to predominate in a given field.<sup>4</sup> Other considerations which affect corrosion rates include temperature and pressure, which determine the nature of the fluid (gas, liquid, etc.) on the metal surface, and minor constituents in the liquid water phase. Figure 3.4 shows how complex the determination of corrosivity can be.

### EXTERNAL ENVIRONMENTS

The external environments discussed in this section are not unique to oil and gas production, but much of the information comes from oilfield experience with



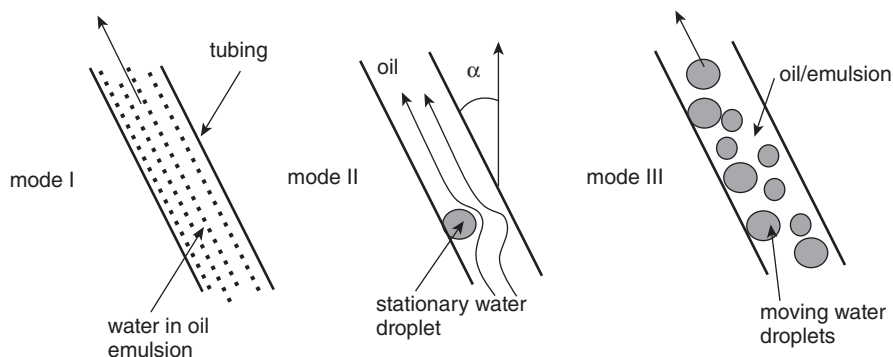


**Figure 3.1** The effects of water cut on the corrosion rate of oil well tubing.<sup>1</sup>

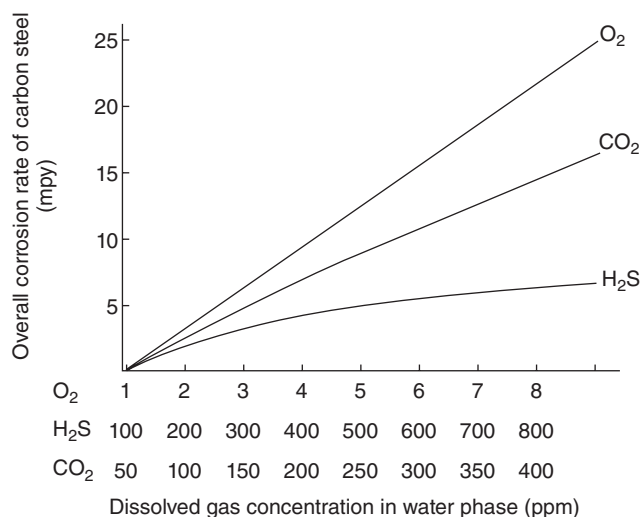
production platforms, buried or subsea pipelines, and similar equipment.

### Atmospheric Corrosion

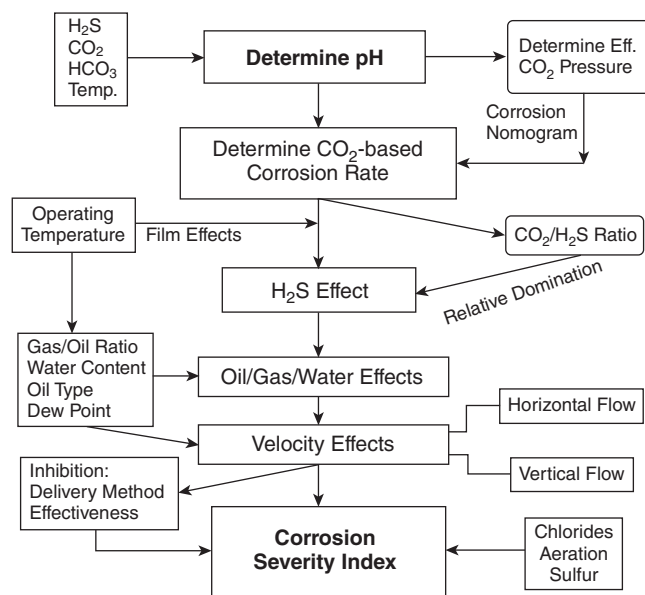
Like all other types of corrosion discussed in this book, this form of corrosion requires the presence of condensed water on the metal surface in order for corrosion to occur. The only exception to this general rule is at very elevated temperatures, for example, those associated with flares and other combustion processes, where corrosion can occur without liquid water. Even here most corrosion occurs below the dew point, because these high-temperature applications require special alloys to withstand corrosion at high temperatures, and this equipment often suffers the worst corrosion during



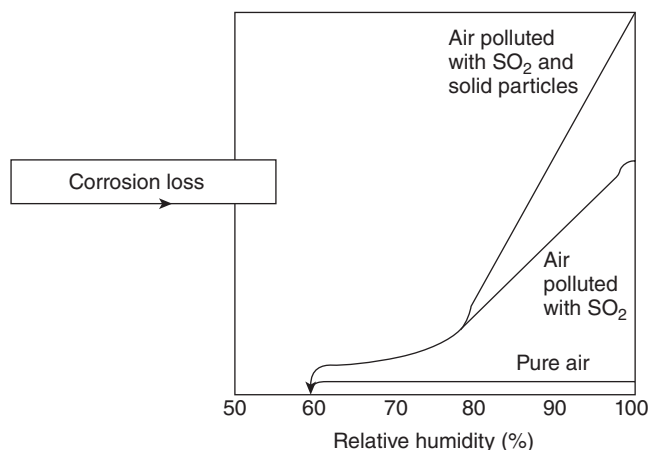
**Figure 3.2** Water wetting producing corrosion on deviated oil wells.<sup>2</sup>



**Figure 3.3** The effect of dissolved gases on the corrosion of carbon steel.<sup>3</sup>



**Figure 3.4** A flow chart indicating the factors which determine the corrosion severity to be expected in an oil or gas field.<sup>5</sup>



**Figure 3.5** Simplified diagram showing the effect of relative humidity and pollution on the corrosion of carbon steel.<sup>6</sup>

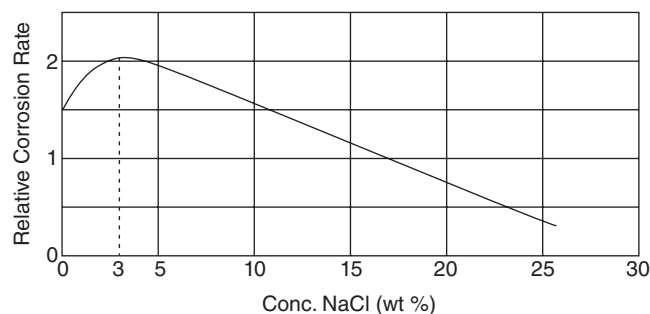
shutdown, when acidic moisture can condense on rough surfaces and cause corrosion similar to that on automotive mufflers during times when the system is cold enough for condensation.

It would seem logical that atmospheric corrosion would not occur until the relative humidity is 100%, but this is not the case. Research dating back to the 1920s has shown that corrosion can occur once the humidity reaches a “critical humidity” of approximately 60–70%.<sup>6–9</sup> Many structures, especially on the away-from-the-sun side (the north side in northern latitudes), stay above this critical humidity virtually all the time, at least whenever the temperature is above freezing.<sup>8</sup> It is important to realize that heat sinks; for example, large structural members on offshore structures can remain below the critical humidity long after the sun comes up and corrosion has diminished elsewhere on the same structure. The presence of deliquescent salts means that many surfaces remain wetted even in sunlight. This is a very important consideration when painting structures, because “flash rusting” due to surface moisture can quickly form and severely degrade the adherence of primary coatings to painted structures (Figure 3.5).

Most metal exposed to atmospheric corrosion is carbon steel, and the most common method of corrosion control is by the use of protective coatings (painting). Some process equipment, storage tanks, and electronic control systems are protected by the use of inerting gases, heaters, deliquescent agents, or vapor phase inhibitors. Control lines, conduit, and similar tubing are often stainless steel on offshore structures.

### Water as a Corrosive Environment

The effect of pH on corrosion of carbon steel was discussed in Chapter 2, Chemistry of Corrosion, figure 2.9.



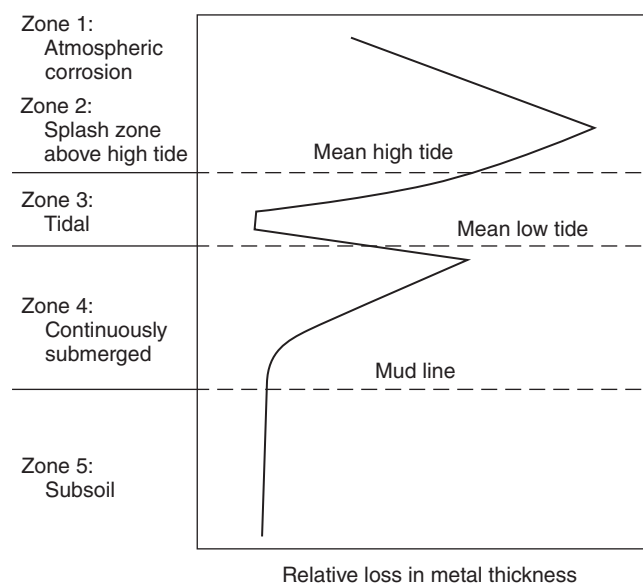
**Figure 3.6** The corrosion rate of iron in air-exposed freshwater at varying salt (sodium chloride) concentrations.<sup>6</sup>

Carbon steel, the most common metal used in oilfield systems, corrodes at unacceptable rates in many aqueous environments, and pH adjustment is a common means of controlling corrosion.

Most readers are familiar with the idea that saltwater is more corrosive than freshwater. The combined effects of dissolved oxygen and salt concentration on the corrosivity of water are shown in Figure 3.6. As increasing amounts of salt are added to water, the electrical conductivity of the electrolyte increases and so does the corrosion rate. At the same time, the oxygen solubility decreases continuously with additional concentrations of salt, and this limits the corrosion rate because oxygen reduction is the rate-controlling chemical (reduction) reaction.<sup>5</sup> The same phenomenon happens with all other salts. The maximum corrosion rate is at approximately 3% salt—the exact concentration depends on temperature and the salt involved.<sup>8</sup> This explains why highly concentrated brines, such as those used in packer fluids, are noncorrosive, provided they are properly pH-adjusted and have little or no dissolved oxygen.

Figure 3.6 explains why freshwater, low in salt, is less corrosive than saltwater, but the most important point to be learned from this picture is that, even at its most corrosive, only about one-third of the corrosion in saltwater is due to salt—most of the corrosion would occur anyway due to the presence of oxygen.

Many reports on corrosion ascribe corrosion damage to the presence of chlorides, the most common anions found in seawater and often found in freshwater as well. This dates back to analytical chemistry practices in the early twentieth century, when qualitative analysis techniques (methods of determining the presence of various chemicals in the environment) were relatively new. The field methods for identifying chloride were relatively easy, and many authors started blaming chlorides for damage caused by salts. It was unnecessary to identify the other components of salt, as there will always be cations (positively charged ions) present to balance the charge of the negatively charged anions. This practice



**Figure 3.7** Zones of corrosion for steel piling in sea water.<sup>10,11</sup>

continues. Any highly ionic salt would cause similar damage, but chloride salts are the most common in most natural environments.

Figure 3.7 shows the corrosion rates of piling in sea-water at various elevations. The highest corrosion rates are in the splash zone, where the metal is frequently covered with air-saturated water. The relatively low corrosion rates in the tidal region are due to the oxygen concentration cells between the highly aerated tidal zone and the fully submerged zone just below. The tidal zone, having high oxygen concentrations, is cathodic to the fully submerged zone just below, which is anodic. As the water deepens, the oxygen concentrations diminish and corrosion decreases.

Produced water can vary from very salty, which is common in oil wells, to almost pure, the condensate associated with some gas wells. This “pure” water can become very corrosive because the dissolved gases,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , plus acidic hydrocarbons can drastically lower the pH, especially at downhole temperatures and pressures.

Most oilfield metal exposed to corrosive waters is carbon steel, and the most common method of corrosion control is by the use of protective coatings (painting) which is often supplemented by cathodic protection. Corrosion inhibitors and corrosion-resistant alloys (CRAs) are also used, especially in downhole environments.

### Soils as Corrosive Environments

Much has been written on corrosion in soils.<sup>12</sup> The definitive work on this subject was published by M. Romanoff

**TABLE 3.1 Corrosivity Ratings Based on Soil Resistivity<sup>13</sup>**

Soil Resistivity (ohm-cm)	Corrosivity Rating
>20,000	Essentially noncorrosive
10,000–20,000	Mildly corrosive
5000–10,000	Moderately corrosive
3000–5000	Corrosive
1000–3000	Highly corrosive
<1000	Extremely corrosive

**TABLE 3.2 Soil pH versus Corrosivity<sup>14</sup>**

pH	Degree of Corrosivity
<5.5	Severe
5.5–6.5	Moderate
6.5–7.5	Neutral
>7.5	None (alkaline)

of the National Bureau of Standards (now the National Institute of Standards and Technology) in 1957 and, when the government report went out of print, it was republished by the National Association of Corrosion Engineers (NACE).<sup>12</sup> Many advances have been made in the understanding of corrosion and cathodic protection since the original publication, but the data represent one of the most extensive sources of corrosion in soil data that is available.

Water and gas occupy much of the space between the solid particles of soil, and these are very important in determining the corrosivity of soils. The air–water interface, wherever located, is the most corrosive location for buried structures, and this location often varies with seasonal rainfall patterns. The minerals in soil dissolve in water and affect the soil resistivity. This directly affects corrosivity, as shown in Table 3.1.

Sandy soils drain well and tend to have the highest resistivities and lowest corrosion rates. Clays that can swell when wetted sometimes produce situations where drainage is prevented and buried structures remain wet and corrode.

Soil pH can also affect corrosion. Table 3.2 shows the effect of soil pH on corrosivity. Acidic soils are encountered in swampy locations, volcanic regions, and areas with silicate rocks and high moisture.

Some dry soil, especially clay-rich soil, contracts during dry seasons as shown in Figure 3.8. This can lead to air ingress down to the buried structure, usually a pipeline, and lead to corrosion when rainy weather returns. Soil expansion and contraction can also cause movement of the buried structure. This produces stresses that can lead to stress corrosion cracking (SCC).





**Figure 3.8** Cracked soil due to drying after the rainy season.

More common is coating damage due to motion of the coated pipeline against rocks and other hard features in the trench.

Peabody, in his classic book on pipeline corrosion, cautioned against galvanic cells between new pipe and old pipe.<sup>15</sup> There are a number of possibilities for galvanic cells to form when a new structure is placed in the soil adjacent to already-buried structures. The most obvious reason for this corrosion is that the lack of soil compaction over the recently disturbed soil is more likely to leave void spaces and locations for enhanced air and moisture ingress. The new structure usually acts as an anode, indicating that increased moisture permeability is corrosion rate controlling.

Buried pipelines are in disturbed soil near soil that has been in place for many years. The differences in aeration and moisture are evident in the vegetation patterns over many pipelines. This is shown in Figure 3.9, which shows two obvious right-of-way locations, each of which has several parallel buried pipelines.

The most corrosive location in any buried structure is usually where the structure crosses the air-to-soil interface. This is shown in Figure 3.10. It is important to concentrate inspections in these locations because cathodic protection, which protects buried structures, cannot be effective in the loosely compacted soil at these locations. Abrasion, motion due to solar-induced expansion and contraction, and a variety of other factors, are likely to cause coating damage at these locations.

Virtually all oilfield equipment buried in soil is protected by a combination of protective coatings supplemented by cathodic protection. The exceptions are in those rare locations where the resistivity of the soil is so high that corrosion is unlikely and cathodic protection would be difficult to achieve. Even in these locations, it is common to use protective coatings. Cathodic protec-



**Figure 3.9** Differences in vegetation over two parallel pipeline rights of way.

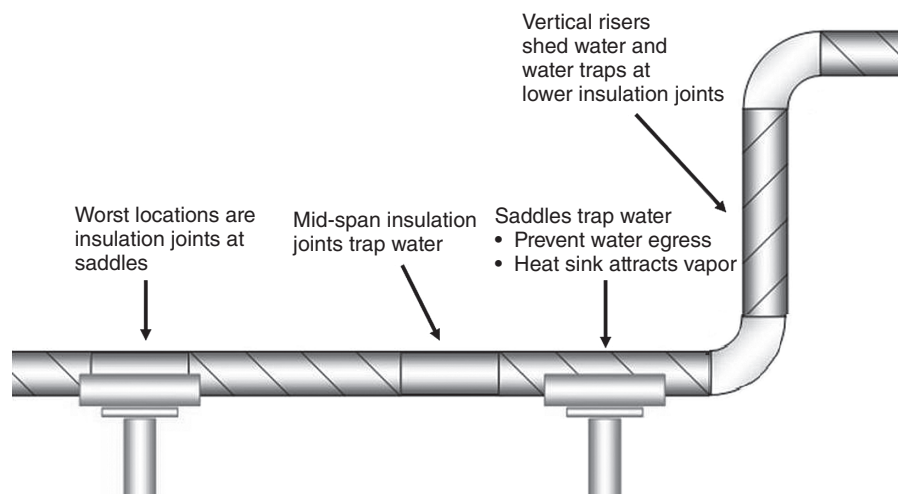


**Figure 3.10** Corroded pipeline at the air-to-soil interface.

tion also cannot work at elevated temperatures where any moisture in the soil will quickly evaporate and no electrolyte is available. Many locations where this occurs, for example, in acidic volcanic soils, require specialized protective coatings, and the lack of widely accepted coatings for these applications is a continuing problem for many operators.

### Corrosion under Insulation

Corrosion under insulation (CUI) is an increasingly important problem. Most air-exposed insulated piping and vessels are covered with porous insulation that is protected from moisture by sheet metal covering. Figure 3.11 shows the corrosion locations identified by a major operator. They are virtually identical to the



**Figure 3.11** Problem locations for insulated above-ground pipelines.

locations discussed in NACE RP0198, *The Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach*, which contains detailed discussions on how this corrosion occurs and approaches to minimize it.<sup>16</sup>

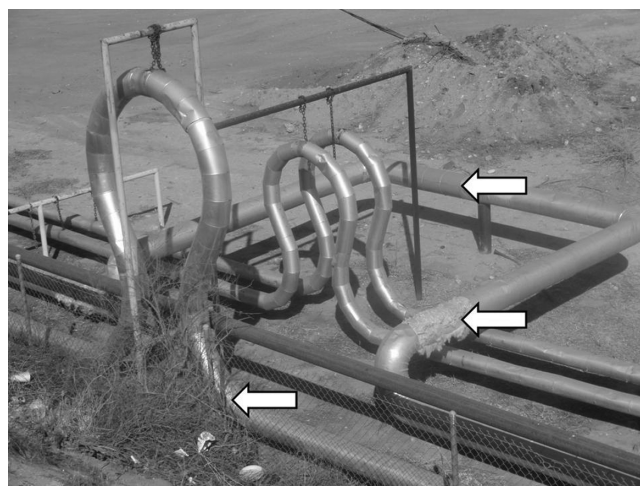
Breaks in the weather barrier usually occur at joints and allow water into the insulation. This water can leach contaminants from the insulation which are then concentrated and deposited on hot surfaces. This can eventually lead to SCC, especially with insulations containing soluble chloride salts.

Corrosion under insulation is hard to inspect, and it is important to conduct these inspections on a frequent basis. It is also important to replace the weather barriers after the inspection. A missing weather barrier is shown in Figure 3.12.

Slugging may occur at the bottom of upstream locations on vertical expansion joints like those shown in Figure 3.12. This creates fluid flow problems, but it also induces stresses into the system and may lead to corrosion fatigue failures. All expansion joints, whether horizontal or vertical, are locations where corrosion and crack detection inspections should be concentrated.

Buried or submerged thermally insulated piping relies on protective coatings for corrosion control. The application of cathodic protection to thermally insulated structures has not worked in most instances.<sup>17</sup>

In addition to the proper design of moisture shields and draining for insulated piping, many operators have adopted the practice of always coating the carrier piping (even if it is made from a corrosion-resistant alloy) with an immersion-grade coating. It is also important to provide inspection capabilities for insulated piping. This is becoming an increasingly important consideration as more and more subsea pipelines are insulated to main-

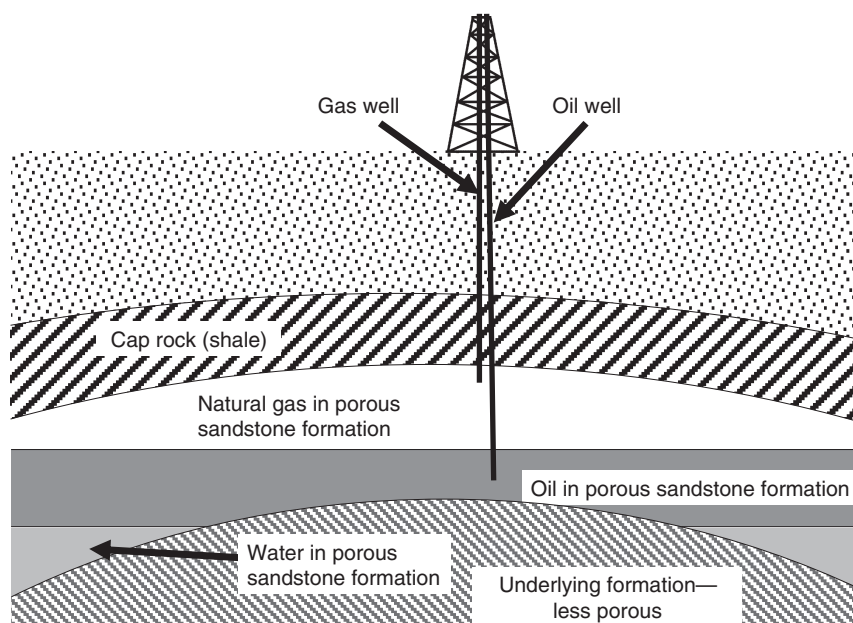


**Figure 3.12** Vertical expansion loops in steam piping for secondary recovery. Top arrow indicates where repair has been covered with painted sheet metal, middle arrow indicates location where sheet metal outer covering is missing, and bottom arrow indicates the bottom of a vertical expansion loop that may cause internal slugging problems, especially with low-quality steam.

tain noncorrosive temperatures on the inside of pipelines and gathering lines that would otherwise quickly cool to the temperatures of the ambient seawater environments.

## INTERNAL ENVIRONMENTS

The environments discussed in this section relate to internal corrosion in oilfield production and piping systems. These internal environments will vary depend-



**Figure 3.13** A typical oil and gas field.

ing on production fields under consideration. Figure 3.13 shows a typical production field where oil and gas wells may be located.

### Crude Oil

Crude oil is not generally corrosive, but the minor constituents found with crude oil can cause corrosion if they separate into the water phase. The viscosity of crude oil also affects water dropout and surface wetting, which affect corrosion.

Oil is a generally benign environment for most metals. Corrosion of oil-wetted metals is rare, but the impurities that are present in oil, especially those which make any water that may be present acidic, can cause severe corrosion. For this reason, it is common practice to try and keep walls of containers oil-wet whenever possible. This is done by such means as insuring that the oil is flowing fast enough to cause turbulence and create an emulsion, a mixture of the immiscible water and oil fluids, which will keep the surfaces from becoming water wet.

### Natural Gas

Unlike oil wells, which may produce noncorrosive fluids for many years before corrosion becomes a problem, natural gas wells are corrosive from the beginning. This is due to the fact that all natural gases will have at least some associated water, and this water, unlike the brines

associated with oil wells, is usually very pure. This pure water has no natural buffering agents, and it becomes acidic due to the presence of dissolved gases,  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ . Most of the discussion on  $\text{CO}_2$  corrosion is associated with natural gas condensate in gas wells or pipelines. Table 3.3 shows typical compositions for natural gas wells and for natural gas from wells that also produce oil.

Natural gas deposits also produce small amounts of mercury. Offshore gas processing systems remove the mercury before the gas enters aluminum heat exchangers used to cool the gas before sending it to shore. This is less of a problem onshore, because aluminum heat exchangers, used offshore for weight savings, are not common in onshore gas processing plants.

Natural gas contains more than methane, and pipelines frequently develop corrosion problems when the small amounts of water,  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ , and other acid-forming compounds collect on the pipeline walls as temperature and pressure conditions change the farther from the compressor the pipeline progresses. Most of the discussion on  $\text{CO}_2$  corrosion is associated with natural gas condensate in gas wells or pipelines.

### Oxygen

The American Petroleum Institute guidelines on corrosion discuss “sweet corrosion”—corrosion caused by  $\text{CO}_2$ , “sour corrosion”—corrosion caused by  $\text{H}_2\text{S}$ , and oxygen corrosion as the major corrodents found in oil



**TABLE 3.3 Compositions of Typical Natural Gas Wells**

Natural Gas	
<i>Hydrocarbon</i>	
Methane	70–98%
Ethane	1–10%
Propane	Trace–5%
Butanes	Trace–2%
Pentanes	Trace–1%
Hexanes	Trace–1/2%
Heptanes +	Trace–1/2%
<i>Non-hydrocarbon</i>	
Nitrogen	Trace–15%
Carbon dioxide <sup>a</sup>	Trace–5%
Hydrogen sulfide <sup>a</sup>	Trace–3%
Helium	Up to 5%, usually trace or none
Gas from a Well That Also Produces Petroleum Liquid	
<i>Hydrocarbon</i>	
Methane	45–92%
Ethane	4–21%
Propane	1–15%
Butanes	1.5–7%
Pentanes	Trace–3%
Hexanes	Trace–2%
Heptanes +	None–1.5%
<i>Non-hydrocarbon</i>	
Nitrogen	Trace–up to 10%
Carbon dioxide <sup>a</sup>	Trace–4%
Hydrogen sulfide <sup>a</sup>	None–trace–6%
Helium	None

<sup>a</sup> Occasionally natural gases are found which are predominantly carbon dioxide or hydrogen sulfide.

and gas production.<sup>18</sup> As discussed in Chapter 2, Chemistry of Corrosion, corrosion cannot occur unless a chemical is available to be reduced at the same time that metal is oxidized, or corroded. The most common chemical that serves this purpose is oxygen, which makes up 20% of the air that we breathe and is found in most soil and liquid environments. The maximum solubility level of oxygen in surface waters is only 8 ppm, but, as shown in Figure 3.2, oxygen is so corrosive that the effects of oxygen can overwhelm the effects of CO<sub>2</sub> and H<sub>2</sub>S, which are less corrosive.

Gaseous oxygen is not naturally present in geological formations that produce hydrocarbons, but once these hydrocarbons reach the surface, oxygen can leak into them and make them corrosive, especially if water separates out as a separate phase.

As the ability to detect dissolved oxygen improved, it became apparent to the oil and gas industry that corrosion problems start if oxygen levels as low as 50–100 ppb are exceeded. This requires careful control

of surface fluids and the use of chemical oxygen scavengers.

Oxygen also reacts with dissolved metal ions, usually iron or manganese in water, and produces suspended solids which can be erosive and clog filters.

Rod-pumped oil wells and low-pressure gas production systems, where compressors can suck air into the system, are common situations where oxygen-induced corrosion is a problem. Air frequently enters tanks with varying liquid levels. Inert gas blanketing can minimize this. Oxygen corrosion is also a problem in water-flood injection equipment.<sup>18</sup>

Most operators have found that the best way to prevent oxygen corrosion is by keeping oxygen out of their systems. This is cheaper than treating the problems that oxygen causes. This requires careful maintenance of seals, valves, and other locations where air and oxygen can leak into the system. Keeping a positive pressure on equipment is another effective means of oxygen exclusion. Inert gas blankets are used over storage tanks. Other methods include corrosion inhibitors, to include oxygen scavengers, protective coating, and cathodic protection of water-wetted interior surfaces of process vessels and storage tanks. CRAs are also used, but this is more common for other corrosive environments and is not often necessary for oxygen corrosion.<sup>18</sup>

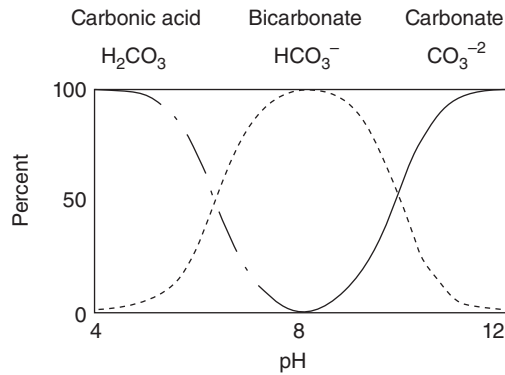
## CO<sub>2</sub>

CO<sub>2</sub> is not corrosive provided it stays dry. Mixing CO<sub>2</sub> with water produces carbonic acid that can be very aggressive in some circumstances. Steel in CO<sub>2</sub>-containing environments forms scales which can be protective, but this scale often breaks down. Figure 3.14 shows how the carbonate–bicarbonate–carbonic acid equilibrium shifts with pH. This picture is for standard temperature (25°C–77°F), but the principle is valid for downhole and pipeline conditions as well. At high pHs, carbonate films will form on metal surfaces, and at low pHs, the bare metal will be exposed to liquid acids.

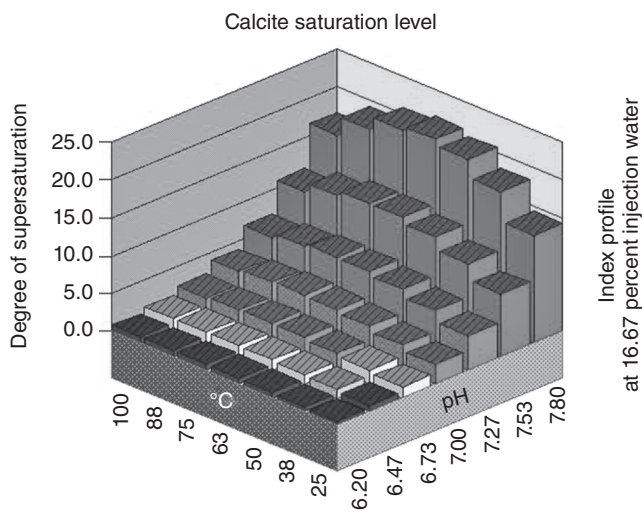
The solubility of carbonate scales and films varies with temperature and pH. This is shown in Figure 3.15, which is produced by one of the numerous software packages used to predict corrosive conditions in oilfield equipment.

Software packages, like the one that produced Figure 3.15, are available that predict the stability of carbonates under a variety of conditions. Corrosion rates are strongly affected by temperature, pressure, scaling tendency, and dissolved gases.

Figure 3.16 shows a sucker rod made of an iron–chrome alloy that corroded when the “protective” scale broke down locally and allowed the underlying metal to



**Figure 3.14** Carbonic acid, bicarbonate ion, and carbonate distribution as a function of pH.



**Figure 3.15** Effect of pH and temperature on the scaling tendency of calcium carbonate.<sup>19</sup> Figure courtesy of FrenchCreek Software—Downhole SAT.

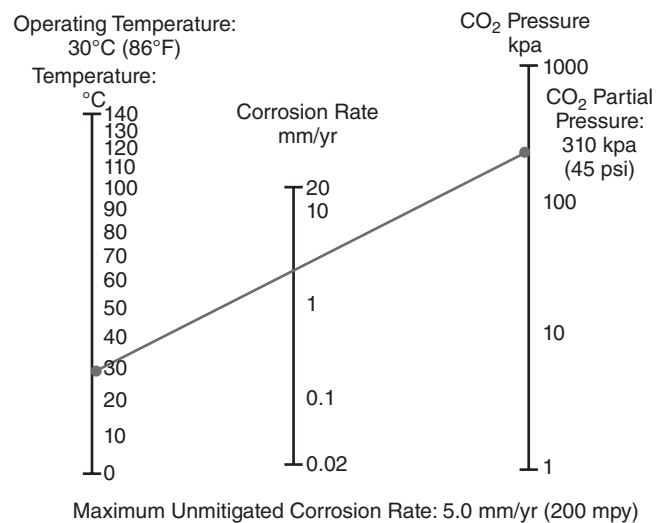
be exposed to aggressive carbonic acid. Relatively clean circular pits surrounded by unattacked metal characterize  $\text{CO}_2$  corrosion. The clean pits and sharp edges of the pits have earned this corrosion the term “mesa corrosion,” because a cross section of the metal looks like the flat-topped mesa (table) mountains common in the southwestern United States.

$\text{CO}_2$  corrosion has become increasingly important in recent years because many deep, hot gas wells have high concentrations of  $\text{CO}_2$ . Figure 3.17 is a nomogram developed by deWaard and Milliams to predict corrosion rates in the presence of  $\text{CO}_2$ . The same research group published the information in Figure 3.18, which shows the effects of liquid velocity of  $\text{CO}_2$  corrosion.

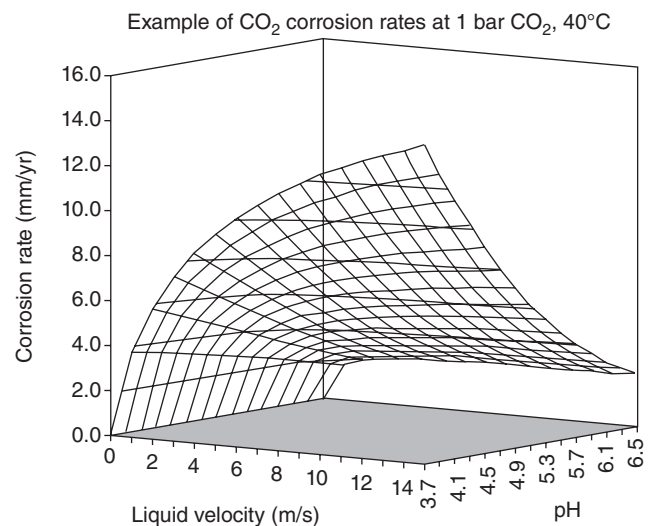
The deWaard-Milliams model used to generate Figure 3.17 is available as an algorithm and is particularly easy to use:



**Figure 3.16** Mesa corrosion on a sucker rod.



**Figure 3.17** Nomogram used to predict corrosion rates in  $\text{CO}_2$ -containing environments.<sup>20</sup>



**Figure 3.18** The effect of liquid velocity on  $\text{CO}_2$  corrosion.<sup>21</sup>



$$\text{Log}(V_{\text{cor}}) = 5.8 - 1710/(273 + t) + 0.67 \log(P_{\text{CO}_2}) \text{ (mm/yr)} \quad (\text{Eq. 3.1})$$

where

$V_{\text{cor}}$  = corrosion rate (mm/yr)

$t$  = temperature, °C

$P_{\text{CO}_2}$  = carbon dioxide partial pressure, bar

This equation is intended for the initial corrosion rate of carbon steel in 5% brine, before the development of protective carbonate corrosion product films that passivate the surface. Nevertheless, the deWaard and Milliams equation is considered a landmark in the estimation of  $\text{CO}_2$  corrosion rates and is widely used to judge the potential severity of  $\text{CO}_2$  corrosion. Note that this equation takes into account both temperature and  $\text{CO}_2$  partial pressure. It is much better than the old rules of thumb based only on  $\text{CO}_2$  pressure.

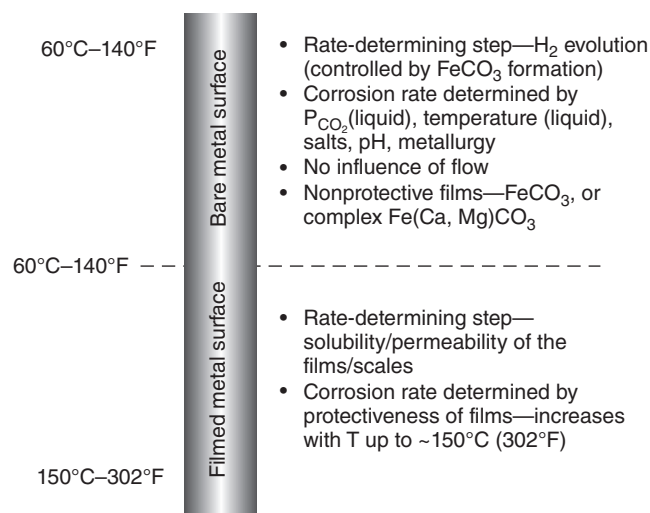
Subsequent modifications by deWaard and Lotz have applied a number of correction factors to the equation to make it more realistic for long-term exposures. These include correction factors for:<sup>21–23</sup>

- Corrosion product films, especially at temperatures above 60°C, where reduced solubility of iron carbonate causes stable corrosion product film formation on the surface
- pH, including the well-known effect of the presence of organic acids in gas condensate
- Effects of system pressure on the fugacity of  $\text{CO}_2$
- Top-of-the-line corrosion for water condensing on the upper walls of the pipe
- Glycol and methanol effects
- Crude oil effects
- Velocity
- Inhibition

These effects have been discussed for many years, and the results of modeling effort, have been to quantify the information that had been applied by rules of thumb in the past. Figure 3.19 shows temperature effects and why they occur.

This discussion has concentrated on the modeling efforts by deWaard and coworkers, but there are numerous other models available.<sup>22–27</sup>

$\text{CO}_2$  or “sweet corrosion” is most often controlled by the use of corrosion inhibitors, but this may not work at elevated temperatures. At one time, 9% chromium steel was used for downhole tubing, but SCC problems developed, and this use has been discontinued. Martensitic stainless steels (12% chromium and higher)



**Figure 3.19**  $\text{CO}_2$  rate-determining factors at various temperatures.<sup>24</sup>

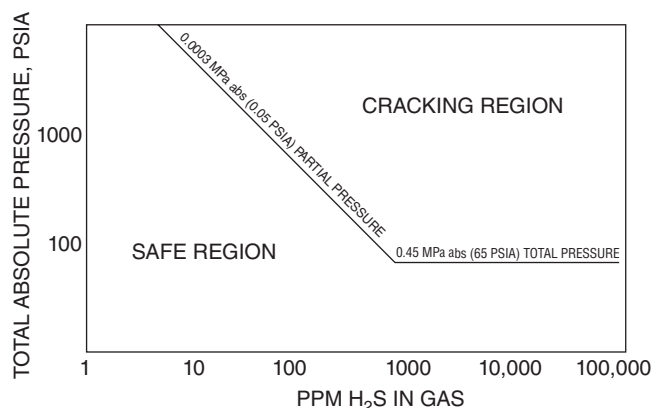
and other CRAs have been successfully used in recent years, especially as downhole temperatures have increased to levels where organic chemical-based corrosion inhibitors cannot be used. Drilling fluid corrosion is often controlled by pH control with caustic soda (sodium hydroxide).

## $\text{H}_2\text{S}$

Oil and gas that contain sulfur are termed sour gas or sour crude, and the most common form of sulfur is  $\text{H}_2\text{S}$  gas.<sup>18,28</sup> Sour conditions can come from  $\text{H}_2\text{S}$  in the producing formation or from surface sources (injection water, lift gases, etc.).  $\text{H}_2\text{S}$  is toxic, and releases of  $\text{H}_2\text{S}$  can cause death within seconds. It also forms a weak mineral acid that can lower pH and make the environment acidic, similar to the effect of  $\text{CO}_2$ . Sulfur is also involved in the metabolism of some microorganisms, and the presence of  $\text{H}_2\text{S}$  can be associated with microbially influenced corrosion (MIC).

$\text{H}_2\text{S}$  can also lead to several forms of metal cracking, variously termed sulfide stress cracking (SSC), hydrogen stress cracking (HSC), hydrogen-induced cracking (HIC), SCC, stress-oriented hydrogen-induced cracking (SOHIC), etc.<sup>28</sup> This is generally a more serious problem, as all forms of environmental cracking can produce sudden gas releases and their associated safety problems.  $\text{H}_2\text{S}$  serves as a hydrogen-entry promoter, and steels that are subject to any form of hydrogen-related cracking are more likely to do so in the presence of  $\text{H}_2\text{S}$ .

Long-life oilfield equipment should be designed for sour conditions even if the production starts out non-corrosive. The souring of many fields is sometimes



**Figure 3.20** Sulfide stress cracking in sour gas environments. Simplified version of figure A-1, NACE MR0175-03.

attributed to surface-water injection or reinjection, but there are other causes as well.<sup>4,29,30</sup>

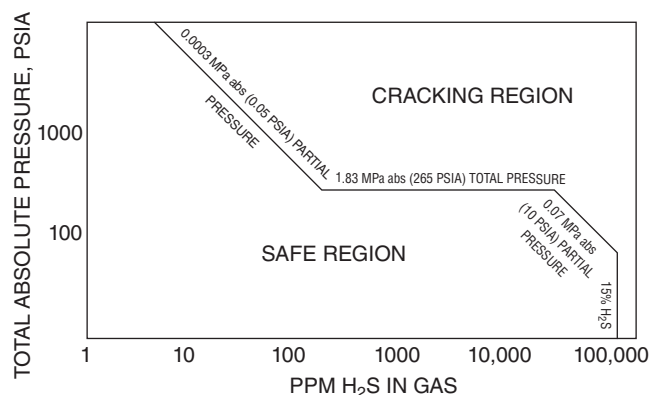
**NACE MR0175/ISO15156—Materials for Use in  $H_2S$ -Containing Environments in Oil and Gas Production** Problems with cracking of various types led to the development of NACE MR0175, which was extensively modified to become NACE MR0175/ISO15156 in 2003.

The original 1975 document, based on work by various NACE and other working groups, covered only valves and wellhead equipment, but the scope was expanded in later revisions. It described various environments where  $H_2S$  cracking was considered to be a problem and placed restrictions, based on temperature and pressure, on where carbon steel could be used in these environments.<sup>31</sup> At temperatures and pressures where carbon steel was deemed unsuitable, the use of CRAs was indicated. The document underwent various changes over the years, driven, in part, by the increased temperatures and  $H_2S$  partial pressures encountered

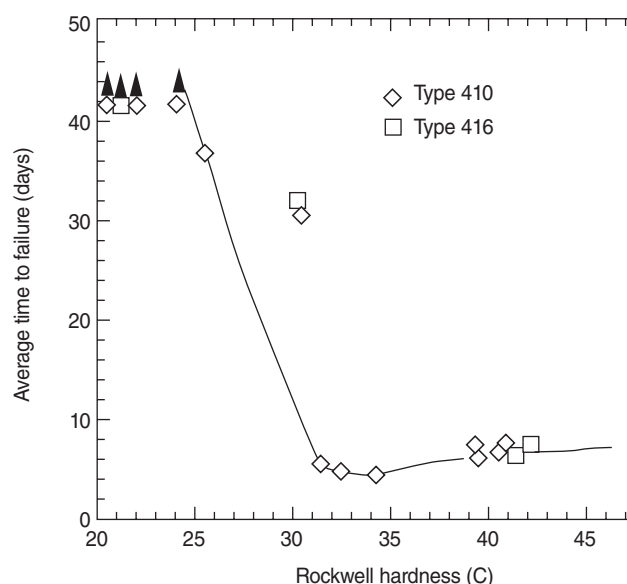
Early versions of the MR0175 had figures like Figures 3.20 and 3.21. These figures clearly showed where MR0175-qualified alloys were required and where the  $H_2S$  and total pressures were low enough that  $H_2S$ -related cracking was considered unlikely.

The original 1975 version of MR075 also restricted the hardness of metals to no greater than HRC 22. This was based on a series of experiments conducted by a consortium of oil companies that showed that the time to cracking in  $H_2S$  environments was very short for harder steels and that softer steels did not tend to crack under the test conditions (Figure 3.22).

Many existing oil and gas fields were designed based on the guidelines in the early versions of this and other international standards. Various problems with MR0175 and conflicts with other international standards, along



**Figure 3.21** Sulfide stress cracking in sour multiphase systems. Simplified version of figure A-2, NACE MR0175-03.



**Figure 3.22** The effect of hardness on time to failure in  $H_2S$  environments.<sup>32</sup>

with ongoing research, lead to a major revision of MR0175 and to the publication of joint standards as NACE MR0175/ISO15156, which was issued in three separate parts and became effective at the end of 2003.

Milliams and Tuttle reviewed the development of the original NACE MR0175 and other  $H_2S$ -related materials standards.<sup>31</sup> They also explained how the new MR0175/ISO15156 documents were organized into the following parts:

**Part 1**—General principles for the selection of cracking-resistant materials

**Part 2**—Cracking-resistant carbon and low-alloy steels

**Part 3**—Corrosion-resistant CRAs and other alloys.

**TABLE 3.4 Equipment Covered by MR0175/ISO15156 Parts 2 and 3<sup>33,34</sup>**

NACE MR0175/ISO 15156 Is Applicable to Materials Used for the Following Equipment	Permitted Exclusions
Drilling, well construction, and well-servicing equipment	Equipment only exposed to drilling fluids of controlled composition <sup>a</sup> Drill bits Blowout preventer (BOP) shear blades <sup>b</sup> Drilling riser systems Work strings Wireline and wireline equipment <sup>c</sup> Surface and intermediate casing Sucker rod pumps and sucker rods <sup>d</sup> Electric submersible pumps Other artificial lift equipment Slips
Wells, including subsurface equipment, gas lift equipment, wellheads, and Christmas trees	Crude oil storage and handling facilities operating at a total absolute pressure below 0.45 MPa (65 psi)
Flowlines, gathering lines, field facilities, and field processing plants	Water-handling facilities operating at a total absolute pressure below 0.45 MPa (65 psi)
Water-handling equipment	
Natural gas treatment plants	
Transportation pipelines for liquids, gases, and multiphase fluids	Lines handling gas prepared for general commercial and domestic use Components loaded only in compression
For all equipment above	

<sup>a</sup> See NACE MR0175/ISO 15156-2: 2003. A.2.3.2.3 for more information.

<sup>b</sup> See NACE MR0175/ISO 15156-2: 2003. A.2.3.2.1 for more information.

<sup>c</sup> Wireline lubricators and lubricator connecting devices are not permitted exclusions.

<sup>d</sup> For sucker rod pumps and sucker rods, reference can be made to NACE MR0176.

The new standard gives requirements and recommendations for the selection and use of cracking-resistant alloys for equipment used in oil and gas production and in natural gas treatment plants. It does not cover refinery equipment. It supplements, but does not replace, other codes, standards, or regulations, and it does not address corrosion except as it is related to cracking.

Table 3.4 shows the types of equipment covered by MR0175/ISO15156. The same table appears in both Part 2, which covers carbon steel and low-alloy steels, and Part 3, which covers CRAs.

*Part 1—General Principles for the Selection of Cracking-Resistant Materials* The scope of MR0175/ISO15156 is applicable to materials used for the following equipment:<sup>33</sup>

- Selection of materials based on the guidance in Parts 2 and 3.
- Qualification and selection of materials for specific H<sub>2</sub>S environments not covered in Parts 2 and 3.
- Determination of qualifications for existing equipment that is to be exposed to an increased level of H<sub>2</sub>S.

- Qualification for service may be based on laboratory testing or field experience.

*Part 2—Cracking-Resistant Carbon and Low-Alloy Steels<sup>34</sup>* The severity of the environment is determined in accordance for carbon, and low-alloy steel will be assessed using Figure 3.23.

The key to this figure is:

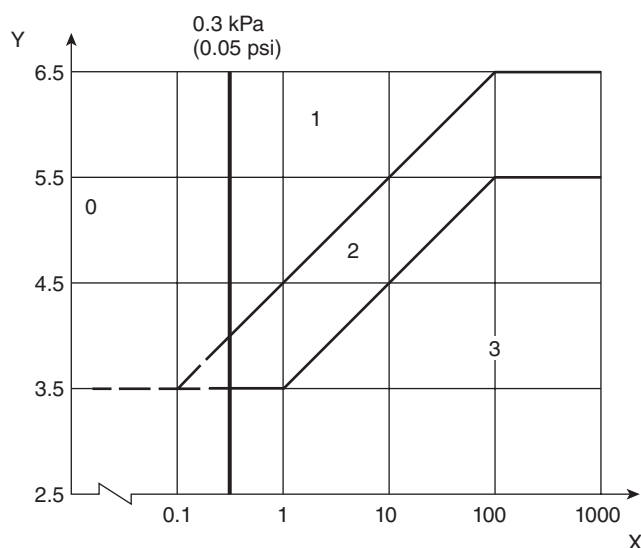
X = H<sub>2</sub>S partial pressure, kPa

Y = *in situ* pH

Appendix D of Part 2 has a detailed discussion of how *in situ* pH is determined, including a number of tables to aid in this determination.

In Region 0 ( $P_{H_2S} < 0.3 \text{ kPa}$  [0.05 psi]), no precautions are normally necessary, but factors that can affect steel performance should be considered:

- Steels susceptible to SCC and HSC may crack.
- Very high strength steels can suffer HSC without the presence of H<sub>2</sub>S. Yield strengths above 965 MPa (140 ksi) may need special processing to ensure that these steels do not suffer HSC or SCC in Region 0 environments.



**Figure 3.23** H<sub>2</sub>S environment classifications for selection of carbon and low-alloy steels.<sup>34</sup>

Regions 1, 2, and 3 define conditions of increasing severity. The types of materials likely to be suitable in these environments are discussed.

**Part 3—CRAs and Other Alloys**<sup>35</sup> Susceptibility to cracking produces restrictions on what alloys can be used in H<sub>2</sub>S environments. Other important variables in H<sub>2</sub>S environments include salt (expressed as chlorides), temperature, and P (total and H<sub>2</sub>S).

Part 3 classifies CRAs into the following categories:<sup>35</sup>

- Austenitic stainless steels
- Highly alloyed austenitic stainless steels
- Solid-solution nickel-based alloys
- Ferritic stainless steels
- Martensitic stainless steels
- Duplex stainless steels
- Precipitation-hardened stainless steels
- Precipitation-hardened nickel-based alloys
- Cobalt-based alloys
- Titanium and tantalum

Copper and aluminum can be used without restrictions on P<sub>H<sub>2</sub>S</sub>, Cl<sup>-</sup>, in *in situ* pH.

Then there are general restrictions based on the alloys, usually by group, and also additional materials selection tables for these applications:

- Casing, tubing, and downhole equipment
  - Downhole tubular components
  - Packer and other subsurface equipment

Gas lift equipment

Injection tubing and equipment

Downhole control line tubing and downhole screens

- Wellheads, Christmas trees, valves, chokes

Wellhead and tree components (with various specified exclusions)

Valves and choke components (with various specified exclusions)

Shafts, stems, and pins

Non-pressure-containing internal-valve, pressure-regulator, and level-controller components

- Process plant

Compressor components

- Materials selection tables for other equipment

Instrument tubing and associated compression fittings, surface control line tubing and surface screens

Springs

Diaphragms, pressure measuring devices, and pressure seals

Seal rings and gaskets

Snap rings

Bearing pins

Miscellaneous equipment as named in the tables (including hardware [e.g., set screws], downhole and surface temporary-service tool applications)

Then the various alloys have individual tables, for example, Table 3.5, which shows the environmental and materials limits for martensitic stainless steels used for equipment. Other tables are more complex and have different limits for various components.

These general limits are then supplemented by tables showing limits for specific applications, such as those shown in Table 3.6.

In the past it has been common practice for operating companies to require that equipment suppliers deliver equipment and supplies in compliance with NACE MR0175 or other similar documents. Older equipment may not meet the more stringent requirements of MR0175/ISO15156.

**Control of H<sub>2</sub>S Corrosion and Cracking** The amount of H<sub>2</sub>S in drilling fluid environments is usually controlled by pH control using caustic soda (sodium hydroxide) and the use H<sub>2</sub>S scavengers. At one time, these scavengers were zinc-based minerals, but concern with environmental pollution has led to nonmetallic

**TABLE 3.5 Environmental and Materials Limits for Martensitic Stainless Steels Used for Any Equipment or Components<sup>35</sup>**

Individual Alloy UNS Number	Temperature Max. °C (°F)	Partial Pressure		pH	Sulfur-Resistant?	Remarks
		H <sub>2</sub> S, pH <sub>2</sub> S Max. kPa (psi)	Chloride Conc. Max. mg/L			
S41000, S42000, J91150, J91151, J91540, S42400	See remarks	10 (1,5)	See remarks	≥3,5	NDS <sup>a</sup>	Any combinations of temperature and chloride concentration occurring in production environments are acceptable.
S41425	See remarks	10 (1,5)	See remarks	≥3,5	No	

These materials shall also comply with the following.

- Cast or wrought alloys UNS S41000, J91150 (CA15), and J91151 (CA15M) shall have a maximum hardness of 22 HRC and shall be
  - austenitized and quenched or air-cooled,
  - tempered at 621°C (1150°F) minimum, then cooled to ambient temperature, and
  - tempered at 621°C (1150°F) minimum, but lower than the first tempering temperature, then cooled to ambient temperature.
- Low-carbon, martensitic stainless steels, either cast J91540 (CA6NM) or wrought S42400, shall have a maximum hardness of 23 HRC and shall be
  - austenitized at 1010°C (1850°F) minimum, then air- or oil-quenched to ambient temperature,
  - tempered at 649°C–691°C (1200°F–1275°F), then air-cooled to ambient temperature, and
  - tempered at 593°C–621°C (1100°F–1150°F), then air-cooled to ambient temperature.
- Cast or wrought alloy UNS S4200 shall have a maximum hardness of 22 HRC and shall be in the quenched and tempered heat-treatment condition.
- Wrought low-carbon UNS S41425 martensitic stainless steel in the austenitized, quenched, and tempered condition shall have a maximum hardness of 28 HRC.

<sup>a</sup> No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment. UNS, Universal Numbering System; NDS, no data submitted; HRC, Rockwell hardness scale C.

**TABLE 3.6 Environmental and Materials Limits for Martensitic Stainless Steels Used as Downhole Tubular Components and for Packers and Other Subsurface Equipment<sup>35</sup>**

Specification/ Individual Alloy UNS Number	Temperature Max. °C (°F)	Partial Pressure		pH	Sulfur-Resistant?	Remarks
		H <sub>2</sub> S, pH <sub>2</sub> S Max. kPa (psi)	Chloride Conc. Max. mg/L			
ISO 11960 L-80 Type 13 Cr, S41426, S42500	See remarks	10 (1,5)	See remarks	≥3,5	NDS <sup>a</sup>	Any combinations of temperature and chloride concentration occurring in production environments are acceptable.

For these applications, these materials shall also comply with the following.

- UNS S41426 tubular components shall be quenched and tempered to maximum 27 HRC and maximum yield strength 724 MPa (105 ksi).
- UNS S42500 (15 Cr) tubing and casing is acceptable as Grade 80 [SMYS 556 MPa (80 ksi)] only and shall be in the quenched and double-tempered condition, with a maximum hardness of 22 HRC. The quench and double-temper process shall be as follows:
  - austenitize at minimum 900°C (1652°F), then air- or oil-quench;
  - temper at minimum 730°C (1346°F), then cool to ambient temperature; and
  - temper at minimum 620°C (1148°F), then cool to ambient temperature.

<sup>a</sup> No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment. UNS, Universal Numbering System; NDS, no data submitted; HRC, Rockwell hardness scale C.





**Figure 3.24** Calcite (left) and gypsum (right) scale in production tubing.

scavengers in recent years. In production tubing, the use of corrosion inhibitors is the normal means of corrosion control. Flowlines and pipelines use a combination of corrosion inhibitors and  $H_2S$  scavengers. Some flowlines and pipelines use internal coatings—either organic or cementitious.<sup>18</sup>

Cracking control in  $H_2S$  requires the selection of the appropriate alloys in accordance with the guidance of NACE MR0175-ISO15156.<sup>33–35</sup>

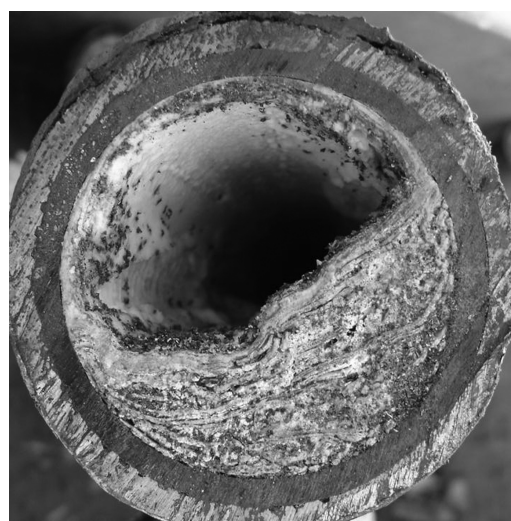
### Organic Acids

Oilfield organic acids sometimes cause oilfield corrosion.<sup>36–38</sup> Like most organic compounds, they tend to be covalent and form weak acids. Their presence is most important at high pressures in gas condensate environments. Many operators have software packages that include organic acids in their downhole pH calculations.

### Scale

Solids in oil and gas production can include both produced solids that are entrained in the oil and gas and scales such as calcium carbonate, calcium sulfate, barium sulfate, and silicates that form on tubing walls and surface equipment as a result of changes in chemistry, temperature, and pressure as fluids are produced, separated, and transported. These scales tend to form on any surface, to include production tubing, sand, and topside piping wherever the temperature and pressure conditions are such that dissolved mineral solubility limits are exceeded.

Figure 3.24 shows scales that formed on the inside of production tubing. As can be seen, these scales can substantially reduce the flow cross section, and eventually, they could plug the pipes. Similar problems occur within producing formations and are the reason why acidizing treatments are sometimes necessary to reopen plugged formations.



**Figure 3.25** Boiler scale in steam generating piping.

The software package that produced Figure 3.15 is one of many calculation methods used to determine the downhole conditions where this scaling will occur. Similar packages are also used to predict scaling tendencies within formations and to predict the effectiveness of secondary and tertiary (e.g.,  $CO_2$  injection) recovery methods used on aging fields.

Scale generally keeps metals dry and reduces general, or uniform, corrosion. Unfortunately, scale can be imperfect, and corrosion, such as that shown in Figure 3.16, occurs at breaks in the scale. Scale or produced solids can also be abrasive and cause erosion corrosion, especially at wellheads and on surface equipment.

Many operators generate steam for various purposes. The same minerals that can plug production tubing can also plug steam piping if the feedwater treatment procedures are inadequate. Figure 3.25 shows boiler scale, which is a major problem in steam-generating equipment.

The carbonate minerals shown in Figures 3.24 and 3.25 are soluble in mineral acids, and the same mineral acids used for descaling downhole formations can be used to remove scale from the inside of piping. If the acid is left in the equipment too long, or if the corrosion inhibitors added to the cleaning acid are inadequate, then rapid corrosion can occur, resulting in perforated tubing within a matter of hours.

### Microbially Influenced Corrosion (MIC)

MIC is a phenomenon that has been recognized for many years and is the subject of a number of books,<sup>39–48</sup> as well as numerous reports on the subject. It is a growing problem in the oil and gas industry and, unfortunately, many of the problems are introduced by improper water handling of surface waters. One of the problems associated with MIC is that most oilfield engineers and technicians have very little understanding of biology and, therefore, are likely to believe “experts” or “rules of thumb” whether or not they have validity.

A number of terms have been used for MIC including “microbiologically induced corrosion,” “biocorrosion,” and others. NACE standardized on the term MIC in the early 1990s, and this term emphasizes that microbes can increase or decrease corrosion. Both phenomena have been reported, although increased corrosion is obviously of more technical and economic interest.

The following recent developments apply to MIC:<sup>39</sup>

- MIC can occur in environments where corrosion is not expected, for example, in downhole pumping equipment removed from any sources of oxygen or other apparent corrodents.
- MIC corrosion rates can be very rapid.
- Liquid culture techniques, the long-standing standard method of identifying the biological sources of MIC, do not provide accurate assessments of the numbers and types of organisms involved in field situations.
- Mitigation and control strategies have shifted from the widespread use of biocides to manipulation of the environment, for example, introduction of smooth surfaces where biofilm attachment is difficult and MIC is less likely.

MIC is not the only oilfield problem associated with biofilms and bacteria. Table 3.7 shows some of the other oilfield problems caused or accelerated by bacteria.<sup>49</sup>

There are a number of possible mechanisms involved in MIC, and some have been better described than others.<sup>50</sup> Many advocates of MIC claim that whenever high microbe populations are found in the presence of corrosion, this is evidence that MIC caused the corro-

**TABLE 3.7 Examples of Operational Problems That May Be Caused by Bacteria<sup>49</sup>**

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Increased frequency of corrosion failures
Increasing H <sub>2</sub> S concentrations
Reservoir souring
Rapid production decline
Metal sulfide scales
Failure of downhole equipment due to metal sulfide deposits
Inefficient oil/water separation
Inefficient heat exchange
Black water
Black powder in gas transmission lines
Filter plugging
Loss of injectivity

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sion. This is not always the case, and several authors have discussed how MIC can be identified. MIC can be confirmed only when all other possible explanations for the observed corrosion have been eliminated.<sup>41</sup>

MIC occurs within biofilms that form on metal surfaces. These films start out microscopically thin but can become much thicker. It might be more accurate to describe this corrosion as being the result of biofouling, which includes macroscopic growths, for example, mussels and barnacles. One definition of MIC is “an electrochemical type of corrosion in which certain microorganisms have a role, either enhancing or inhibiting.”<sup>40</sup>

Like most other forms of corrosion, MIC is an electrochemical process. Microorganisms can affect the extent and severity of corrosion and, like all organism-related phenomena, water is necessary for microbial life and therefore is necessary for MIC.

Bacteria attach to metallic surfaces and start to form thin biofilms consisting of cells, living or dead. These films also incorporate water and debris from the environment. Growth of these films can change the chemical concentrations of the water at the biofilm/metal substrate interface. Films as thin as 12 μm can prevent diffusion of oxygen and produce localized areas that are anaerobic enough to promote the growth of sulfate-reducing bacteria (SRB). One result of biofilm formation is the creation of concentration gradients that produce electrochemical cells that can be explained by the Nernst equation discussed in Chapter 2, Chemistry of Corrosion.

Biofilms can form in minutes to hours, and MIC can be detected within 10–20 days in stagnant waters, for example, improperly drained and dried equipment that has been hydrotested with microbe-containing water.

There are many ways of classifying bacteria, but two distinctions are important to understand for control of oilfield corrosion:

- Sessile bacteria are attached to surfaces and become motionless.
- Planktonic bacteria freely float or swim in a body of water.

It is relatively easy to sample a fluid for planktonic, free-floating bacteria, but the actions of sessile bacteria are frequently more important in determining corrosion rates. This usually requires insertion of coupons or probes into the fluid at the elevation where the sessile bacteria are most likely to be forming. Sessile bacteria lead to most corrosion problems in oilfield equipment.<sup>49,51</sup> Planktonic bacteria can also produce corrosive chemicals which can lead to corrosion and H<sub>2</sub>S-related cracking.

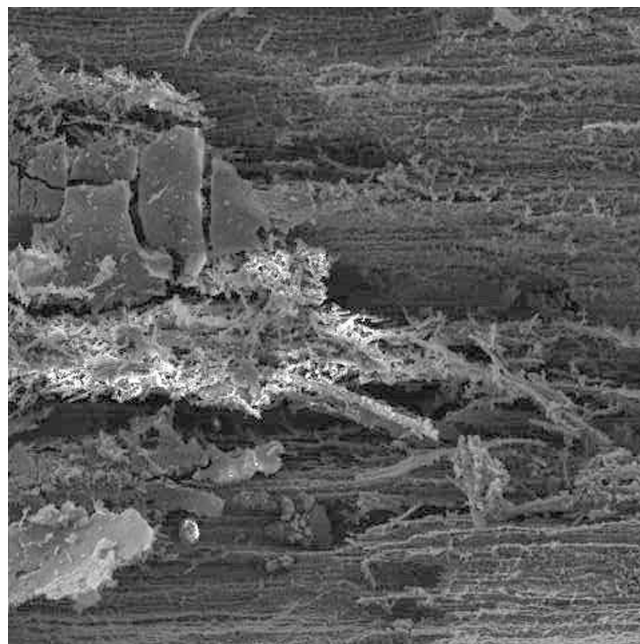
NACE classifies the most important types of oilfield bacteria as:<sup>50</sup>

- SRB
- Iron-oxidizing bacteria
- Acid-producing bacteria (APB)
- Sulfur-oxidizing bacteria (SOB)
- Slime-forming bacteria

Another widely used classification is the distinction between aerobic (air-breathing, more correctly oxygen-breathing) bacteria and anaerobic bacteria, which do not require air or oxygen for their respiration.<sup>39,40</sup>

All of these bacteria contribute to the formation of biofilms, where bacteria can grow (Figure 3.26). These biofilms typically contain from 40% to 60% pore space by volume, and most of this pore space is full of water where the bacteria can find nutrients and reproduce. Biofilms also serve as collection points for larger microbes, fungi, debris, scale precipitates, and other solids that both increase the volume of the biomass and also help to shield the sessile bacteria within the biomass from chemical treatment biocides. Thick biofilms may have different characteristics from the outside, where slime may attract inorganic debris, to the inside, which may become highly acidic, anaerobic environments conducive to growth of SRB populations that lead to further corrosion. These biofilms can be microscopic or macroscopic in nature.

Many authorities claim that SRB are the most important bacteria associated with oilfield corrosion,<sup>50</sup> but this is disputed.<sup>39,40</sup> Nonetheless, SRB are important, are widely studied, and are widely reported. SRB are anaerobic, they do not require dissolved oxygen in their metabolism, but they can tolerate oxygen, usually by becoming dormant and not reproducing in oxygen-rich environments. SRB are typically found in dead legs and other quiescent locations, but planktonic SRB can



**Figure 3.26** Biofilm inside a corrosion pit. Photo courtesy of K. Pytlewski, Anamet, Hayward, California.

survive in turbulent waters and then settle and become sessile when fluid flow diminishes. Most SRB strains thrive at 25–35°C (77–95°F), but some can thrive up to 60°C (140°F).

SRB cause corrosion by oxidizing organic compounds to CO<sub>2</sub> or organic acids. They reduce sulfates and other sulfur compounds to sulfide ions, which can then become gaseous or dissolved H<sub>2</sub>S. Steel corrosion in acids produces monatomic hydrogen atoms at the cathodes. Hydrogen can be reduced by SRB and depolarize metal surfaces. This depolarization increases corrosion rates, especially in corrosion pits.<sup>50</sup> The reaction of H<sub>2</sub>S with dissolved iron ions can also produce iron sulfide scales on nearby surfaces. These scales can alter corrosion rates, either increasing or decreasing corrosion depending on the circumstances.

Iron-oxidizing bacteria (IOB) are also known as iron-depositing bacteria or iron-related bacteria (IRB). They are usually found in mounds, called tubercles, over pits on metal surfaces. The presence of these tubercles is not always due to IOB, but it has been claimed that if the tubercles are shiny, rather than dull, this is a strong indication of IOB-related MIC.<sup>52</sup> Rust-colored water or yellow slime may indicate dissolved oxygen and suspended iron oxides, but it may also indicate the presence of IOB. IOB are found in open ponds, supply wells, filters, piping, equipment, and injection wells.<sup>50</sup>



**TABLE 3.8** Classes of Bacteria Considered to Be Important in Oilfield MIC<sup>52</sup>

Bacteria	Oxygen Requirement	Metals Affected
<i>Desulfovibrio</i>	Anaerobic	Carbon steel, stainless steel, zinc, copper, aluminum
<i>Desulfomonas</i>	Anaerobic	Carbon steel
<i>Thiobacillus thiooxidans</i>	Aerobic	Carbon steel, copper
<i>Thiobacillus ferrooxidans</i>	Aerobic	Carbon steel
<i>Gallionella</i>	Aerobic	Carbon steel, stainless steel
<i>Sphaerotilus</i>	Aerobic	Carbon steel, stainless steel
<i>Pseudomonas</i>	Aerobic	Carbon steel, stainless steel

MIC, microbially influenced corrosion.

IOB oxidize dissolved  $\text{Fe}^{+2}$  ions to  $\text{Fe}^{+3}$ . They can also oxidize  $\text{Mn}^{+2}$  to  $\text{Mn}^{+3}$ . Depending on the pH, these ions may then combine with dissolved anions to form  $\text{Fe}(\text{OH})_3$  or  $\text{FeCl}_3$ , which can then deposit on tubercules sealing them and creating anaerobic conditions conducive to the growth of SRB.<sup>50</sup>

There are many types of APB that can become trapped under biofilms where they create acids leading to underfilm corrosion.

SOB are aerobic. Some react with  $\text{CO}_2$  to produce sulfuric acid,  $\text{H}_2\text{SO}_4$ , which is usually more corrosive than the relatively nonionic and less corrosive  $\text{H}_2\text{S}$  acid formed by SRB.

Some forms of SOB require sunlight for photosynthesis.<sup>50</sup> SOB can exist over a range of pHs from 0–4 but survive best at pHs around 2.5.<sup>50</sup>

Slime-forming bacteria can form capsules over biofilms. These slime capsules can protect the underlying biomass from biocides. They can also create differential aeration cells, and slime-producing bacteria can be either aerobic or anaerobic.<sup>50</sup>

Table 3.8 shows a number of classes of bacteria, their oxygen requirement, the metals they corrode, and the mechanism whereby they are thought to operate.

No unique form of corrosion is associated with MIC; this makes identification difficult. The presence of large amounts of planktonic or sessile bacteria does not necessarily mean that MIC is present. At one time, it was common to analyze corrosion pit morphology (shape, depth, etc.) in an attempt to confirm MIC and identify the types of microbe likely to be involved. This approach has been discredited in recent years.<sup>39,40,51–55</sup> One authority claims that MIC identification requires that all other

possible explanations for the observed corrosion must be eliminated before the problem can be attributed to MIC.<sup>40</sup>

Field personnel often rely on collecting water samples for planktonic bacteria or probes to collect sessile bacteria. They then follow prescribed procedures to allow the growth and identification of the collected bacteria.<sup>56</sup>

Culture methods are commonly applied for detecting and estimating bacterial numbers in the petroleum industry. These methods rely on supplying all the requirements for microbial growth for the bacteria and then use visual means to determine the presence of these bacteria. The media must supply an energy source, a carbon source, trace elements, as well as maintaining the proper pH, temperature, and oxygen requirements for the microorganisms. The method generally used in the field involves the use of small glass bottles containing media sealed with a rubber septum. The sample from the system is injected using a hypodermic needle into the first bottle. After mixing, a diluted sample is withdrawn from this bottle and injected into the next bottle in the series.

Subsequent dilutions are made and the bottles are then incubated and observed at intervals for clouding which would indicate microbial growth. This method is known as the “serial dilution or dilution-to-extinction method” since the first clear bottle indicates how many dilutions are required to achieve an absence of microorganisms in the sample.

The ideal procedure for estimating bacterial numbers is to use a triplicate dilution series then incorporate statistically valid most probable number (MPN) techniques to estimate bacterial numbers. At least a duplicate series of dilutions should be used in order to avoid the possibility of error created by contaminated samples. In practice, however, most oilfield personnel use a single dilution series.

A large number of media are available for performing serial dilution tests. These allow the estimation of numbers of total heterotrophic populations, anaerobic populations, various types of SRB, iron bacteria, and other organisms of interest.

However, it should be kept in mind that culture media detect only the number of bacteria in a sample, which will grow in the culture media. They do not represent an unequivocal estimation of total or specific bacterial numbers.

This method is a powerful tool for investigation of oilfield problems but should not be used as the sole source of information for assessing system characteristics.<sup>57</sup>

The same reference that supplied the quote above quote found that field test kits were unreliable, at least under the conditions tested.

The collection and identification of sessile bacteria is much more difficult than for planktonic bacteria because the locations where sessile bacteria are located can vary, and the types of bacteria under different biofilms within a piping system may also vary.

The following situations and locations are likely to be associated with MIC corrosion problems.

**Stagnant conditions:** Hydrotesting and dead legs are two common sources of MIC problems.<sup>41</sup> Improperly drained hydrotest water can produce measurable corrosion within 2 weeks. Consumption of biocides in dead legs or in low spots of hydrotested equipment cannot be expected to last for extended periods.

**Welds** are locations of surface roughness conducive to the growth of bacterial colonies protected from the action of biocides. Why welds are preferentially corroded by MIC is not completely understood, but there are many reports to indicate that this phenomenon is real.<sup>40,58–60</sup>

**Particulates** are places for bacteria to attach. They also settle in low-velocity locations providing deposits under which biofilms can form and grow. The increased surface area associated with particulate production can also remove biocides from fluids and increase the demand for biocides.

There are many types of equipment that develop MIC problems, but pipelines and piping systems predominate in reports on MIC problems. Any stagnant water location is likely to develop this problem. Improperly treated injection waters are known to produce reservoir souring when surface bacteria proliferate in the downhole or produced water environment.

It is easy for a chemical biocide to kill planktonic bacteria as they are unprotected by scale, debris, or biofilms. In the sessile environment, abrasive pigging as well as chemical biocide treatment may be required to disinfect a system.

Pigging or other mechanical cleaning methods are a prime means of controlling MIC. Biofilms and other deposits on metal surfaces can shield microbes from chemical treatments, and their removal is necessary to insure that piping and similar structures are efficiently treated by biocide injection.

Biocides are used to kill or render harmless biological organisms. Biocides can be either oxidizing or non-oxidizing chemicals. Chlorine, an oxidizing biocide that is often used as a biocide in drinking water, is also used in oilfield waters. It can be released from gaseous chlorine generators, from chemical injection, or by electrolytical chlorine generation. It often produces faster action than nonoxidizing biocides.<sup>50</sup> Unfortunately, chlorine from any source also oxidizes other species

in oilfield brines—organic acids, soluble iron, and  $H_2S$ —and this oxidation can produce solids which must be removed from treated water before injection. Chlorine also responds to the oxygen scavengers used in injection water treatment systems and can accelerate corrosion of metals and degradation of gaskets and seals.

Nonoxidizing biocides are usually more cost-effective in systems with low hydrocarbon contents (injection water and freshwater makeup systems). Most nonoxidizing biocides are filming amines.<sup>51</sup> They can have problems in high-salinity waters and in high-calcium brines.<sup>51</sup> Table 3.9 lists several nonoxidizing biocides and their compatibility with various materials used in their handling and injection equipment.

Many commercial biocides are blends of various chemicals. The reason for this is that different microbes respond to different biocides, and it is virtually impossible to identify all of the microbes present in a given water. These biocides are marketed as “broad-spectrum” biocides and are often quite effective. An alternative to broad-spectrum biocides is alternating biocides with the intention of preventing the buildup of biomasses that are resistant to the biocide being used.

The major problems associated with MIC are in low-flow areas and in places where deposits of any type are allowed to form. Effective treatment for MIC requires mechanical cleaning as well as biocide treatment.

## Mercury

Mercury is an element found in trace amounts in most hydrocarbon formations.<sup>61</sup> It can cause liquid metal cracking problems in brazed aluminum heat exchangers used for offshore gas processing, and this is the reason why mercury removal systems are commonly placed before the aluminum heat exchangers on offshore processing platforms.<sup>62</sup> Mercury forms very inefficient cathodic surfaces when condensed on steel and is not a serious galvanic corrosion problem.<sup>63</sup> The principal threat of mercury, or any liquid metal, is liquid metal embrittlement, a form of SCC.

## Hydrates

Hydrates are ice-like deposits that can form in natural gas systems.<sup>64,65</sup> Methane networks “trap” water and form very hard plugs like those shown in Figure 3.27. Hydrates are a major flow-assurance problem in subsea gas and multiphase pipelines. Thermodynamic inhibitors that lower the temperatures at which hydrates can form, are a common method of preventing hydrate formation in subsea pipelines. The most common

**TABLE 3.9 Compatibility of Common Biocides with Various Metals and Elastomers<sup>49</sup>**

Biocide	Compatible <sup>a</sup>	Incompatible
Quaternary amines	UNS S31603 (Type 316L stainless steel (SS)) Polyvinylchloride Polyolefin PTFE Polyvinylfluoroethylene Perfluoroelastomer Vinyl ester	Carbon steel (CS) Natural rubber Neoprene Acrylonitrile-butadiene rubber (NBR)
Glutaraldehyde	SS Polyethylene Reinforced plastics	CS Galvanized iron Aluminum (Al) Tin (Sn) Zinc (Zn)
Acrolein	SS Butyl rubber Perfluoroelastomer PTFE Polyethylene Polypropylene	Neoprene Fluoroelastomer Acrylonitrile-butadiene rubber (NBR) Polyvinylchloride Polyurethane Galvanized metals
Isothiazolone	UNS S31603 Fiberglass-reinforced epoxy Polyester Vinyl ester Polyethylene Polypropylene PTFE Hydrocarbon rubber Fluoroelastomer Polyphenylene sulfide (PPS)	
THPS	SS Al Polyvinylchloride Nylon PTFE Polyethylene Polypropylene Polyurethane Silicone Fluoroelastomer Nitrite rubber Natural rubber	Copper Brass Mild steel Cast iron Zn
DBNPA	Fluoroelastomer PTFE Polyethylene Polypropylene Polyvinylfluoroethylene Fiberglass-reinforced plastic	Mild steel UNS S30400 (Type 304 SS) Al Nickel (Ni)

Note: Copy of table 3, NACE Publication 31205.

<sup>a</sup> Compatible with field strength product at ambient temperature. Compatibles are typically verified under use concentration and conditions. UNS, Universal Numbering System; PTFE, polytetrafluoroethylene; NBR, synthetic nitrile rubber; THPS, tetrakis (hydroxymethyl) phosphonium sulfate urea polymer.

thermodynamic inhibitors are methanol, monoethylene glycol (MEG), and di-ethylene glycol (DEG). Corrosion inhibitors must be tested for compatibility with these hydrate inhibitors.

### Fluid Flow Effects on Corrosion

Figure 3.28 shows various fluid flow regimes common in oilfield tubing, pipelines, and process equipment. Fluid flow regimes determine where erosion corrosion, under-deposit corrosion, or other forms of corrosion are likely to occur. The flow regimes also determine the type of wetting that occurs, for example, in pipelines and piping

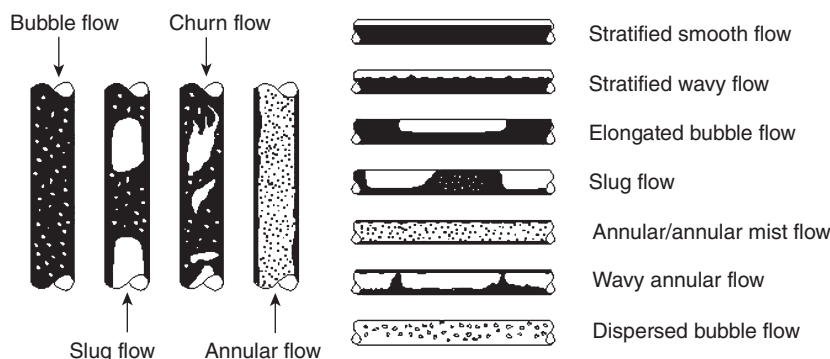


**Figure 3.27** Hydrate plug removed from a subsea pipeline. Photo courtesy of Petrobras, reprinted with permission.

where top-of-the line corrosion may occur due to the presence of corrosion-causing condensation in locations where corrosion inhibitors have not been applied. It would not be unusual for a gas well to progress from single-phased liquid flow at the bottom of a well to single-phased vapor flow as the tubing progressed from temperature and pressure conditions at the bottom of the well to the lower temperatures and pressures near the surface.<sup>65</sup> Additional discussions on fluid flow aspects of corrosion are presented in Chapter 5, Forms of Corrosion, and in Chapter 8, Oilfield Equipment.

### SUMMARY

Oilfield environments vary by location within upstream oil and gas operations. Liquid water wetting is necessary for corrosion, and the solids and gases dissolved in water strongly affect corrosivity. The three primary corrosion problems in oilfield waters are oxygen in surface equipment and  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from production fluids. Crude oil generally produces a benign environment with relatively few corrosion problems until the field ages and the water cut increases to the point that liquid-water wetting starts to occur. In contrast to crude oil, gas wells and piping tend to be corrosive from the beginning. This is due to the relatively low mineral content of condensed waters that allows any dissolved acid gases, usually  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ , to lower the pH and cause corrosion. The presence of scales (mineral deposits on surfaces) and microbes influences corrosion but are less important than the dissolved gases— $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ .



**Figure 3.28** Two-phase fluid flow regimes common in oilfield tubing and piping. The dark areas represent liquid and the light areas are gas.

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# 4

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## MATERIALS

The most important materials used in oil and gas production are carbon steels. Oilfield corrosion control of carbon steels has traditionally used corrosion inhibitors for internal corrosion and a combination of protective coatings and cathodic protection for external corrosion. Starting in the 1980s, many new production environments became too aggressive for this approach, and the use of corrosion-resistant alloys (CRAs) has increased.<sup>1,2</sup> Polymers and flexible polymers, called elastomers, are included in this chapter, but most of the discussion will be concerned with metals.

The discussions of mechanical properties and other properties of metals concentrate on carbon steels, and it is estimated that approximately 90% of all materials used in oilfield applications are carbon steels. This situation is unlikely to change in the foreseeable future. The principles of heat treatment, welding, and other operations for carbon steels are similar to those for other alloys.

The uses of metals and polymers for cathodic protection anodes and for protective coatings are discussed in Chapter 6, Corrosion Control.

### METALLURGY FUNDAMENTALS

Virtually all metals used by industry are alloys. The exceptions are coatings, which sometimes involve commercially pure metals, and conductors. Pure metals are better electrical and thermal conductors than alloys. Strength considerations (stiffness) of heat transfer

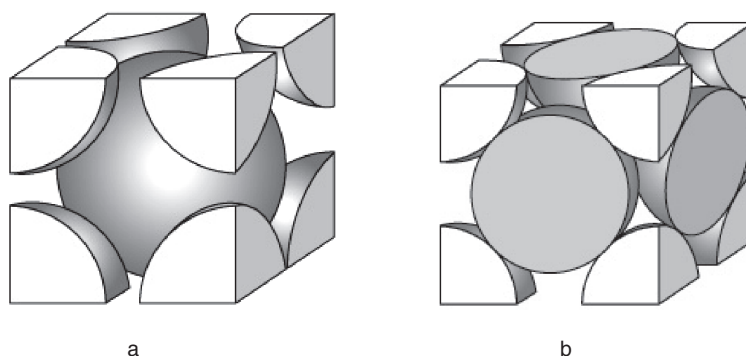
tubing usually means that alloys are used in heat exchangers and similar devices, but pure copper, and sometimes other metals, are used for electrical conductors. These conductors are not unique to oilfield applications and will not be discussed in this book.

### Crystal Structure

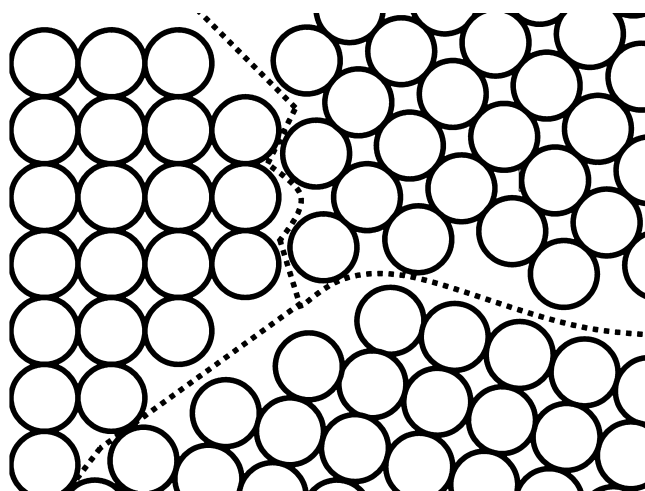
Most solids, with the exception of glasses and organic materials, are crystalline. This means that the atoms in the crystal are arranged in one of seven possible arrangements, only three of which are common in metals. Figure 4.1 shows the two most common crystal arrangements, body-centered cubic (BCC)—found in low-temperature iron, and face-centered cubic (FCC)—found in high-temperature iron, aluminum, and austenitic stainless steel. Zinc and titanium form hexagonal close-packed crystals, but the two crystal systems shown in Figure 4.1 are found in all other oilfield metals.

The type of crystal structure, defects in the crystal structure, and size of the crystals combine to determine the mechanical and, to some extent, corrosion-resistance properties of oilfield alloys. Note how the FCC crystal has 50% more close-packed directions (directions where the atoms “touch” their nearest neighbors) than the BCC crystals. This is why FCC metals, to include high-temperature iron and carbon steel, are both weaker and more ductile than BCC metals.

A solid metal consists of many crystals containing numerous defects. The combination of alloying additions, crystal size, and different crystal structures determines the mechanical and corrosion resistance properties of the alloy. Figure 4.2 shows how three crystals, with different orientations but the same chemistry, join and form grain boundaries. It is obvious that the grain



**Figure 4.1** Crystal structures common in metals: a = body-centered cubic, b = hexagonal close-packed.<sup>1</sup> Source: Callister & Rethwisch, *Fundamentals of Materials Science and Engineering: An Integrated Approach*, 3rd ed., John Wiley & Sons, Inc., 2008.



**Figure 4.2** Grain boundaries in a metal.

boundaries, indicated by dotted lines in Figure 4.2, have larger spaces between the atoms, and this is where impurity atoms are most likely to be located. Unwanted segregation of impurity atoms to grain boundaries can cause major embrittlement and corrosion problems.

A typical crystal has millions of atoms, and the defects in the individual crystals determine some of their mechanical and corrosion resistance properties. Defects in crystalline solids include vacancies—locations where atoms are missing from the crystal, impurities—atoms of different elements than the base metal, and grain boundaries between crystals. These defects affect the mechanical properties and corrosion resistance of metals. Detailed discussions of defects, and how they affect the strength and other properties of metals, are available in metallurgical texts.<sup>3</sup>

Most metals are alloys, deliberate combinations of two or more elements to develop the desired properties. Alloying additions can produce substitutional solid

solutions when the atomic sizes of the solute and solvent atoms are similar (Figure 4.3), or interstitial solid solutions when the alloying addition involves atoms so small that they can fit between the interstitial holes in the parent crystal (Figure 4.4). The solubility limits of interstitial atoms are very low, and this type of solid solution is primarily used for surface hardening of steel using carbon, oxygen, boron, or nitrogen.

If the solubility limits of the secondary atoms are exceeded, a different crystal structure is formed, and this produces a stronger alloy, because atomic motion caused by stresses is impeded whenever the atoms reach a grain boundary and must change direction.

### Strengthening Methods

Metals are strengthened by one of the following strengthening mechanisms:

**Work Hardening** Low-temperature deformation of metals introduces atomic motion that produces crystalline defects, dislocations that strengthen the metal. This works for very thin materials, wire and sheet, but is not practical for thicker metals found in oil country tubular goods (OCTGs), plate, and structural steels.

**Grain Size Refinement** Modern oilfield tubular goods (OCTGs) are often strengthened by the addition of aluminum or other alloying elements that cause finer grain sizes in the finished product.

**Alloying** All metals used for strength are alloys of two or more different elements.

**Second-Phase Hardening** The presence of a second phase having different chemistry and/or crystal structure (usually both) is a major means of strengthening alloys. Carbon steel, the most common structural alloy, is a combination of almost pure iron crystals and other

crystals containing iron carbide particles called cementite because of their hardness.

**Precipitation Hardening** Second phases formed by heat treatment alter the microstructure and produce controlled microstructures with different grain sizes and/or crystals than would occur from chemistry alone.

**Thermomechanical Processing** This is a term that has been applied to oilfield metals in recent years. This is a combination of plastic deformation of the metal and associated heat treatments to develop the optimum properties. It usually involves work hardening, but it can also involve deformation at temperatures so high that work hardening does not occur.

### Mechanical Properties

**Strength** For most applications, the strength of a metal is the most important property. Strength can be defined in a number of ways, but most industrial specifications set targets for yield strength and ultimate tensile strength. Hardness, ductility, and the related property of toughness are also important.

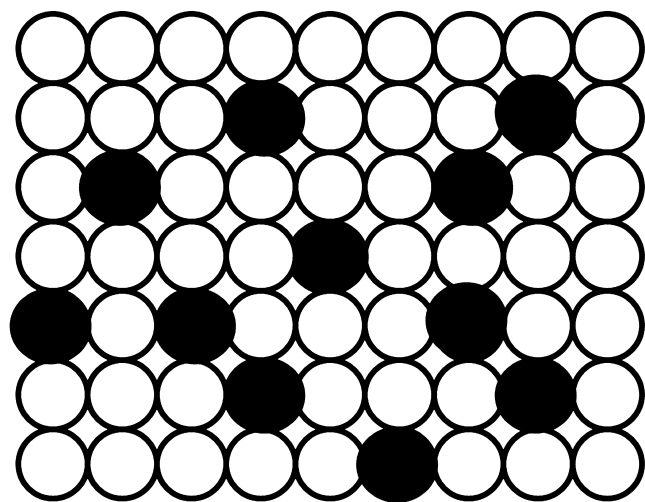


Figure 4.3 Substitutional solid solution in a crystalline solid.

The tensile strength (resistance to elongation) of metals is measured by pulling a standard metal sample like the one shown in Figure 4.5 in tension and recording the elongation of the gauge length in the smallest diameter section, where most of the elongation occurs.

The results are plotted on a stress (load per unit area) versus strain (elongation, usually measured in percent) diagram like Figure 4.6.

From this diagram, the following metal properties can be measured:

The yield stress is the stress at which elastic deformation, stretching of the sample that will recover to the original length of the sample once the load is removed, ceases and plastic or permanent deformation starts to become apparent, and the sample will not return to its original length once the load is removed.

Figure 4.6 shows the stress-strain plot decreasing and then increasing several times in the vicinity of the proportionality limit and yield stress. This is due to the initial unlocking of internal defects called dislocations that are the start of the work-hardening process. The dislocations move by slip at approximately  $45^\circ$  to the tensile axis and may form a phenomenon called Luders bands on the metal surface.<sup>4</sup>

Most engineering design codes require the structure to be loaded to only a fraction of the yield stress

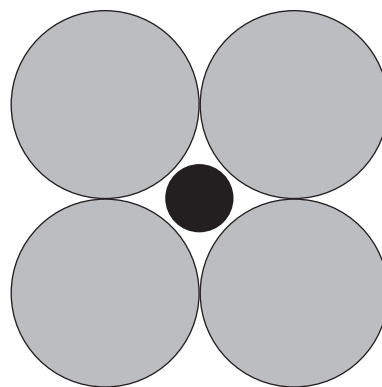


Figure 4.4 Interstitial solid solution in a crystalline solid.

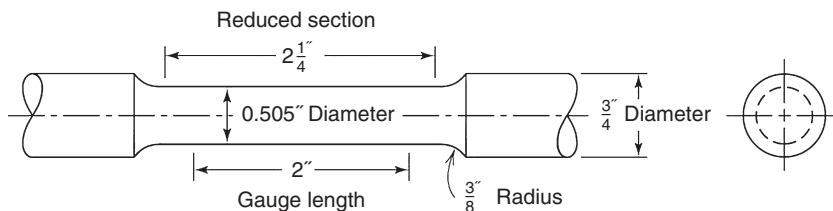
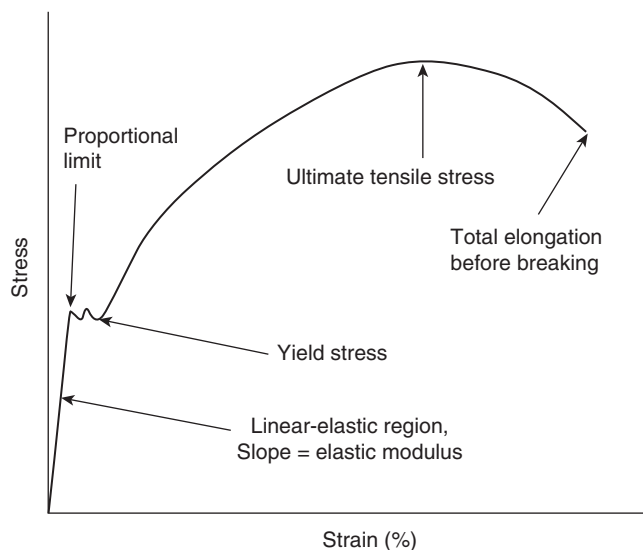


Figure 4.5 Standard sample used for determining the tensile strength of a metal.<sup>3</sup>



**Figure 4.6** Stress-strain curve for low-strength carbon steel showing upper and lower yield stresses.

determined by a safety factor. This is the stress that cannot be exceeding during operation of the structure or equipment in question. Safety factors depend on the type of structure under discussion.

The proportionality limit is almost the same as the yield stress. It is the point on the stress-strain plot where the deformation ceases to be in direct proportion to the stress. Up to this point, the stress strain curve is considered to follow Hooke's Law:

$$\varepsilon = \sigma E \quad (\text{Eq. 4.1})$$

where:

$$\varepsilon = \sigma E$$

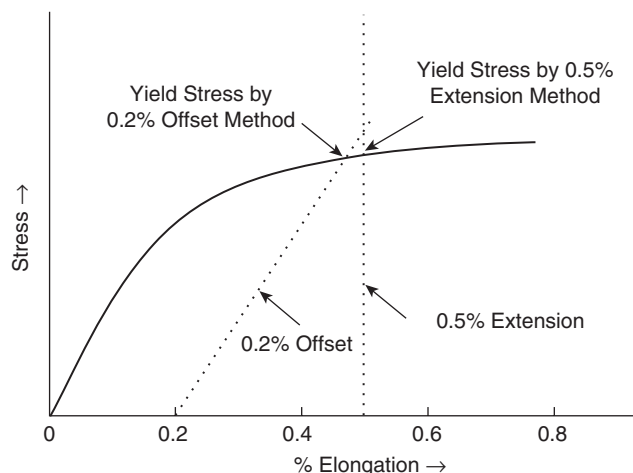
$\varepsilon$  = strain = deformation/original length, normally shown in percent

$$\sigma = \frac{\text{load}}{\text{original cross-sectional area}}$$

$E$  = elastic modulus (Young's modulus).

Beyond the proportionality limit, the stress-strain diagram becomes curved and Hooke's law is no longer obeyed.

The highest point on a stress-strain plot determines the ultimate tensile strength or stress. Once the yield point is exceeded, plastic deformation starts. This results in work hardening. At some point, the reduction in cross-sectional area, and possibly the formation of internal microvoids, lowers the resistance to deformation. The specified minimum (ultimate) tensile strength (SMTS) is included in most materials specifications



**Figure 4.7** Stress-strain diagram comparing 0.2% permanent offset and 0.5% extension methods of determining yield stress.

along with the more important specified minimum yield strength (SMYS).

The elastic modulus is the slope of the straight line of the stress-strain plot before yielding occurs. This is a measure of the interatomic attraction between atoms. For steels, this number is the same at approximately 200 GPa ( $30 \times 10^6$  psi) and does not vary with yield strength or tensile strength. This term is also called Young's modulus, after the nineteenth-century British researcher who developed the concept advancing earlier work by Euler and others.

The total elongation before fracture is the most common measure of the ductility of a metal. This elongation will depend on the size of the tensile sample as well as the material being tested.<sup>4,5</sup>

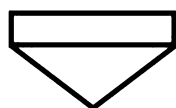
The above concepts were developed and incorporated into design codes before the development of modern measuring devices. It is now recognized that most metals, to include the carbon steels that are the primary alloys used in the oil field, will exhibit some deviation from linear-elastic (Hooke's Law) behavior even at relatively low stresses. Modern methods of determining the yield stress are based on determining the load at which only 0.2% permanent offset (elongation) occurs after the load is released or by measuring the stress necessary to produce 0.5% deformation while the load is applied. The two methods produce similar results, as shown in Figure 4.7, and both are accepted for oilfield materials.<sup>2,5-8</sup> The term "proof stress" is sometimes applied to yield stresses determined by the permanent offset method.

Most materials specifications will define the SMYS and the SMTS. Minimum elongation before breaking, which depends on sample size, may also be specified in addition to properties described below.

**Hardness** Hardness is a material property that is often important, for example, for wearing surfaces. In oilfield practice, it is also used as a convenient method for field inspection of carbon steel products to determine if the metal in question has the necessary strength for the application in question. The hardness of a metal increases as the strength increases, and tables to convert measured hardness into approximate tensile strength are available.

The principle behind hardness testing is very simple. A penetrator of a known hardness, greater than the material being tested, is forced into the sample with a predetermined load. The larger the indentation produced, the softer the sample being tested. A number of hardness testers have been developed, but the Rockwell hardness test, developed in the United States in the early twentieth century, has been the most popular test for steels in North America. Other tests, differing primarily in the shape of the indenter, have gained use in other locations.

NACE (formerly the National Association of Corrosion Engineers) standards for hardness testing originally specified the use of Rockwell hardness testing and, for a long time, HRC—Rockwell hardness using a 120° diamond cone penetrator (Figure 4.8)—was the



**Figure 4.8** Side view of a diamond cone penetrator for Rockwell hardness testing.

standard used for oilfield testing in North America.<sup>4,5,9,10</sup> Other penetrators utilize round spheres (Brinell or Rockwell B) or different-shaped diamond pyramids (Vickers and Knoop).

The most recent revisions of NACE standards for now cite Vickers hardness values, but the American Petroleum Institute (API) standards continue to refer to Rockwell hardness test. Conversion charts to compare the results of the various testing methods are available, but the user is cautioned that these conversions may be inaccurate, and the material in question should be tested with the hardness tester stated in the appropriate materials specification.<sup>4,5</sup> Table 4.1 shows some conversions between different hardness tests and the approximate tensile strengths of carbon steels associated with various levels of hardness.

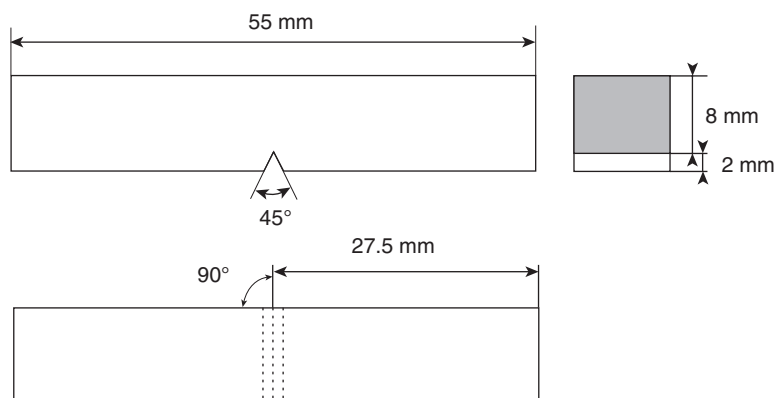
NACE MR0175/ISO15156 and other standards have used hardness values, which are easily confirmed in the field and are usually considered to be nondestructive tests, to determine if metals can be used in H<sub>2</sub>S-containing oilfield environments.<sup>11–13</sup>

It is unfortunate that yield strengths, which are much more widely used instead of tensile strengths in materials specifications, are not readily available in tables like Table 4.1. Craig has suggested a “rule of thumb” that for carbon and low-alloy steels, the yield strength is approximately 75–90% of the tensile strength.<sup>2</sup> A recent publication by researchers at the Colorado School of Mines has suggested some yield strength correlations, but this recently published data have not yet met widespread acceptance for oilfield applications and standards.<sup>14</sup>

**TABLE 4.1 Carbon Steel Hardness Values and Approximate Yield Strengths**

Rockwell				Brinell		Vickers or Firth Diamond Hardness Number	Tensile Strength	
Diamond Brale			1/16" Ball	10m/m Ball				
150 kg C Scale	60 kg A Scale	100 kg D Scale	100 kg B Scale	3000 kg Load  Diameter of Ball Impression in mm	Hardness Number		ksi	mPa
30	65	48	105	3.6	285	302	142	979
29	65	47	104	3.65	277	294	138	951
28	64	46	103	3.7	269	286	134	923
27	64	45	103	3.75	262	279	131	903
26	63	45	102	3.8	255	272	126	869
25	63	44	101	3.8	255	266	124	855
24	62	43	100	3.85	248	260	122	841
23	62	42	99	3.9	241	254	118	813
22	62	42	99	3.95	235	248	116	800
21	61	41	98	4	229	243	113	780
20	61	40	97	4.05	223	238	111	756

Adapted from: Material Hardness Conversion Table, [http://www.corrosionsource.com/handbook/mat\\_hard.htm](http://www.corrosionsource.com/handbook/mat_hard.htm), July 2009.

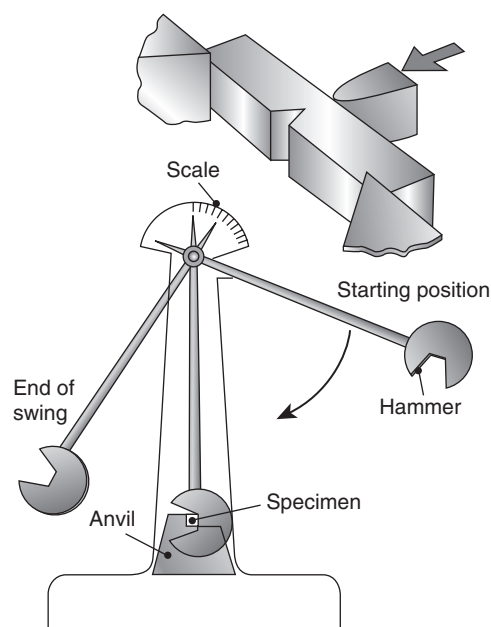


**Figure 4.9** Charpy V-notch impact test specimen.

**Ductility** Ductility is usually considered to be the ability of a metal to be stretched in tension before fracture. API Specification 5CT for oilfield tubing and casing requires a minimum elongation, depending on sample thickness, of between 8% and 30%. The minimum elongation depends on the sample size and the strength of the metal, with stronger metals having less ductility.<sup>4,5</sup> In addition to elongation before breaking, some definitions of ductility specify the reduction in cross-sectional area at fracture as a measure of ductility. The opposite of ductility is brittleness. Some authorities consider any metal to be brittle that has less than 5% elongation before breaking.<sup>3</sup>

**Toughness** Toughness is a measure of the resistance of a material to impact loading. This is an important materials property that has been gradually recognized by the petroleum industry and has been added to many materials specifications and design procedures. The mechanical properties described in previous paragraphs are measured at relatively low strain rates. Materials also need to withstand shock loading, and this can be measured by a number of different techniques. The most common technique is the Charpy impact test. Figure 4.9 shows a typical Charpy impact specimen. The specimen, with a premachined notch so that it will break at the desired location, is loaded into a low-friction pendulum apparatus (Figure 4.10) and is struck with a known standard impact energy. The energy absorbed when the sample is impacted and breaks is then measured by determining the difference between the potential energy before releasing the pendulum and comparing it with the potential energy at the end of the swing. The difference in elevation is directly proportional to the energy absorbed in breaking the sample.<sup>15</sup>

BCC metals, including carbon steels, become brittle when cold, and this can become a major problem for



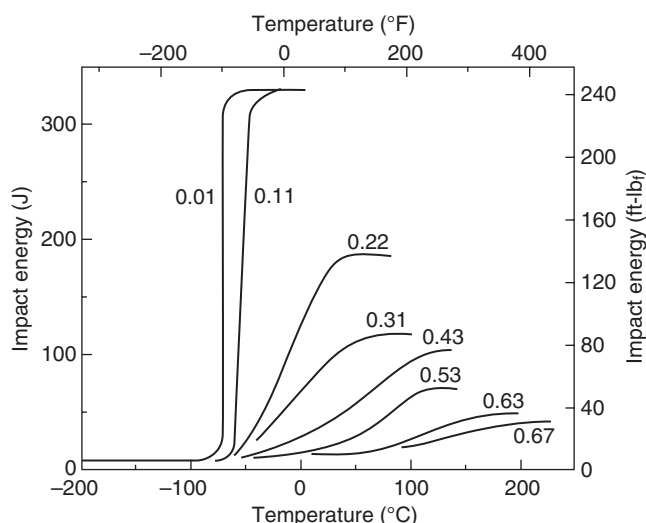
**Figure 4.10** Charpy V-notch impact tester.

some applications or locations. FCC metals tend to be ductile at all temperatures used in oil and gas production, and this is the reason why aluminum, stainless steel, and iron-nickel alloys (e.g., 9 Ni) are used for liquefied natural gas (LNG) storage and piping. Figure 4.11 shows a plot of ductile-brittle transition temperatures for a series of carbon steels. As the carbon content, and the strength and hardness increase, the transition temperatures decrease.

Table 4.2 shows ambient temperature (21°C, 70°F) impact resistance requirements for drill pipe. Similar requirements have been introduced for other OCTGs in recent years.

Carbon steel ductile-brittle transition temperatures (DBTTs) are affected by many parameters, but grain





**Figure 4.11** Influence of carbon content on the Charpy V-notch energy-versus-temperature behavior for steel.<sup>3</sup>

**TABLE 4.2** Impact Energy Requirements for Carbon Steel Drill Pipe<sup>16</sup>

Specimen Size	Minimum Average Charpy V-Notch Impact Energy of Each Set of Three Specimens		Minimum Charpy V-Notch Impact Energy of Any Specimen of a Set	
	Ft-lb	Joules	Ft-lb	Joules
10 × 10	40	54	35	47
10 × 7.5	32	43	28	38
10 × 5.0	22	30	19	26

size is probably one of the most important.<sup>2</sup> Grain size refinement for line pipe and other OCTGs has been introduced in recent years, and this has improved several properties to include toughness and DBTTs.

## Fracture

Materials fracture when they are overloaded. The forms of fracture for many metals are:

**Overload (ductile) fracture or deformation:** This is relatively uncommon in upstream operations. Conservative safety factors predominate in most designs and pressure relief systems also help. Drill pipe and sucker rod strings may have this problem on occasion.

**Creep:** Creep is the elongation of a material over time without an increase in loading. It is not

common in upstream oilfield operations, but it is a significant concern in refineries, which operate at very elevated temperatures.

**Brittle fracture:** This is common in Arctic service but can also occur due to cooling caused by expansion of released gases (Joule-Thompson cooling) from natural gas pipelines and other pressure vessels.

**Fatigue:** Fatigue is a common problem in sucker rod strings and rotating equipment. Concerns about low-cycle fatigue limit the number of runs for tubing strings used for downhole inspection.

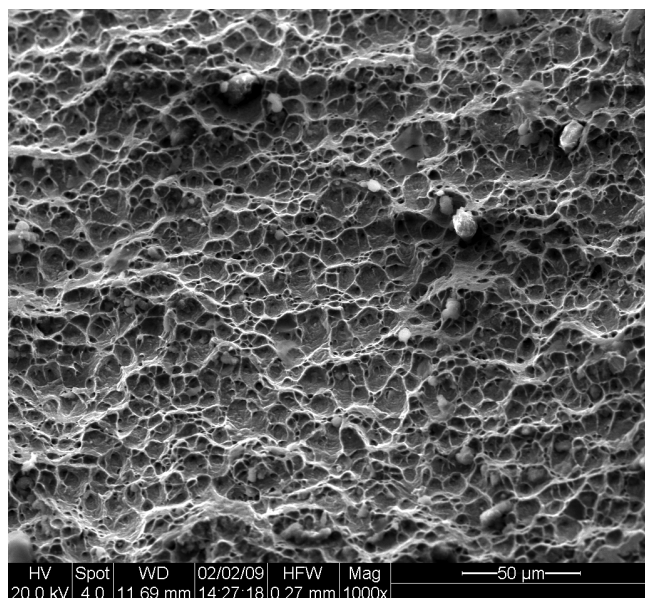
**Ductile Fracture** Ductile or overload fracture is the result of exceeding the strength of the material. Bulging or bending is a frequent warning that overload failures are about to occur as the load exceeds the material's yield stress and plastic deformation begins. Water hammer is one example where this warning may not be present before the final overload failure. This can be a problem in piping systems with slug flow.

Ductile fracture is accompanied by plastic deformation. This can be seen macroscopically and, under the scanning electron microscope, looks like Figure 4.12. Notice the curved surfaces where plastic deformation produced microscopic voids that formed and grew together before the final overload failure.

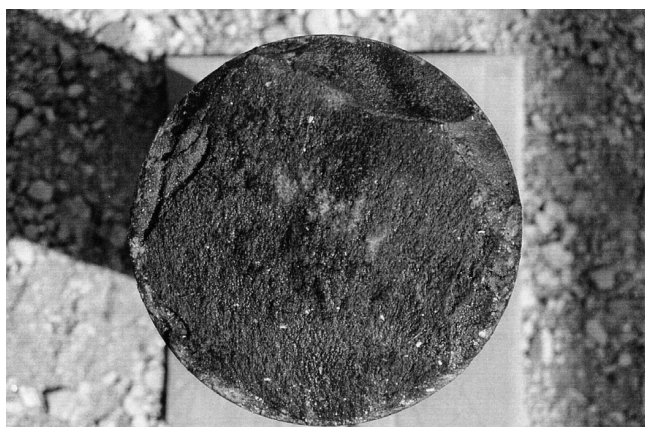
**Brittle Fracture** Brittle fracture absorbs very little energy, as shown in Figure 4.11. The surfaces of a brittle failure are flat and do not show the curvature due to plastic deformation typical of ductile failures shown in Figure 4.12. Figure 4.13 shows the flat surface of a valve stem that was incorrectly heat-treated to excessive hardness which resulted in this brittle failure. The very flat surface is characteristic of brittle failures.

Close examination of brittle fracture surfaces shows that the brittle fracture tends to occur along well-defined crystallographic directions. This cleavage fracture tends to produce smooth and shiny surfaces, unlike the dull gray surfaces usually seen with ductile fractures.<sup>18</sup> The cleavage planes are easily seen in scanning electron microscopes, which have the advantage of high-depths of field as well as the ability to image surfaces at high magnifications. This is shown in Figure 4.14, which shows a brittle fracture surface due to stress corrosion cracking. The cleavage in Figure 4.14 is either between crystals (intergranular fracture) or along certain planes within the individual crystals (transgranular fracture). This transition from intergranular to transgranular fracture is common on many brittle fracture surfaces.<sup>18</sup>

A major problem with brittle fractures is that once they reach a critical flaw size, they spread at the speed of sound. This means that inspection for the defects that



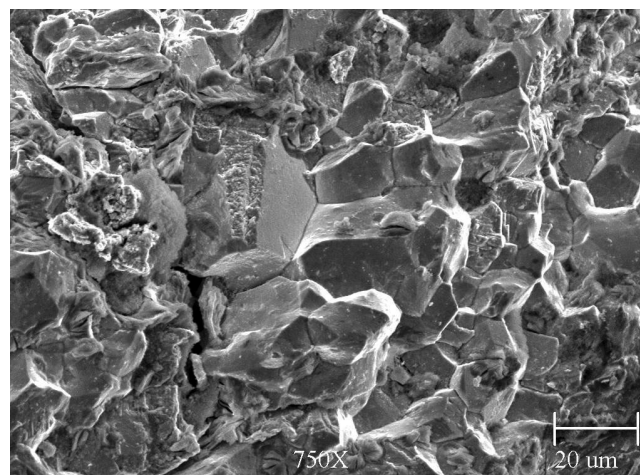
**Figure 4.12** Ductile fracture surface. Photo courtesy of A. Michaels, Forensic Materials, San Jose, California.



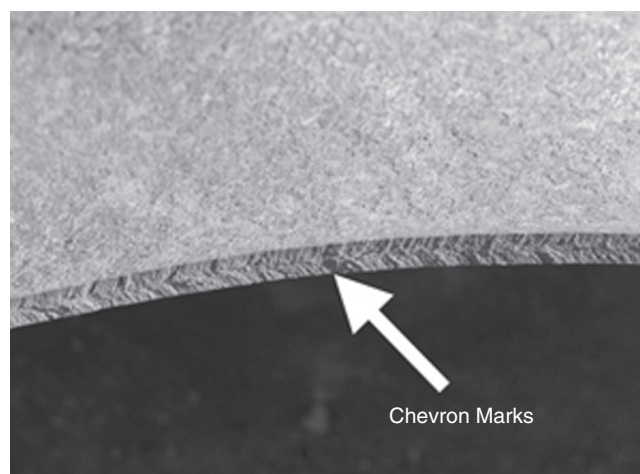
**Figure 4.13** Brittle flat fracture surface on incorrectly heat-treated valve stem.<sup>17</sup>

start brittle fractures is very important. Once the cracks start to run, it is too late to prevent major damage. Figure 4.15 shows the chevron patterns characteristic of brittle fracture propagation. These markings, which are left on the surface of brittle fractures in both metals and polymers, point to the origin of the crack and are useful in failure analysis. Identifying why the crack started in the first place is often necessary in order to insure that the repair or replacement does not suffer the same fate.

Brittle fracture can result from stress corrosion cracking and hydrogen embrittlement, from improper welding procedures or heat treatment, from low temperatures that cause metals to become brittle, from the presence of sharp defects (stress risers), and from other



**Figure 4.14** Brittle fracture surface showing flat and angular surfaces. Photo courtesy of J. Ribble, Materials Evaluation & Technology Corporation, <http://www.metco-ndt.com>.



**Figure 4.15** Chevron marks on the surface of a brittle fracture. Photo courtesy of R. Craig Jerner, PhD, PE, J.E.I. Metallurgical, Inc., Dallas, Texas, <http://www.metallurgist.com>.

causes. Figure 4.11 shows how carbon steels become brittle, less able to absorb impact loads, at different temperatures depending on carbon contents, which affect the strength and hardness levels.

Engineers must take ductile-brittle transformation temperatures into account when designing equipment. This means that the equipment must be designed in accordance with the following concepts:

**Minimum design metal temperature (MDMT):** This is the lowest temperature expected in service, including consideration for operating temperature, operational upsets, autorefrigeration, atmospheric temperature, and any other sources of cooling.



**Design minimum temperature (DMT):** This is the API term for the American Society of Mechanical Engineers (ASME) MDMT. They are the same, but specifiers should be careful which code (API or ASME) a pressure vessel or other equipment must meet.

**Critical exposure temperature (CET):** This is the lowest temperature the equipment will see under “significant stress,” which in most cases is assumed to be 8 ksi (55 MPa).<sup>19</sup>

**Minimum allowable temperature (MAT):** The lowest permissible temperature limit for a material at a specified thickness based on the material’s resistance to fracture. This is the lowest safe temperature for the equipment in question.

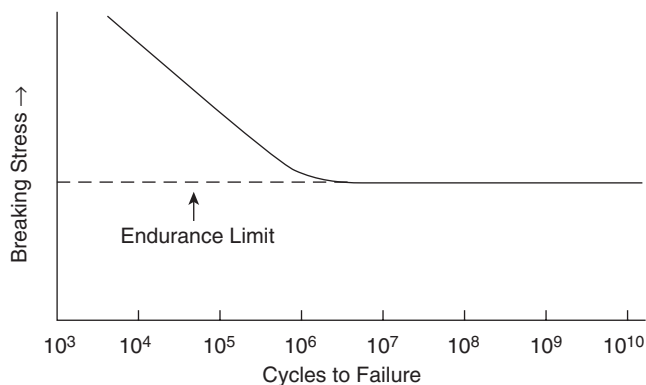
The lowest temperature expected in service is the CET, and it must always be above the MAT, which is the lowest temperature the equipment in question can safely handle.

Detailed discussions on the above-listed temperature concepts are available in pressure vessel and piping reference books and design codes.<sup>19–26</sup>

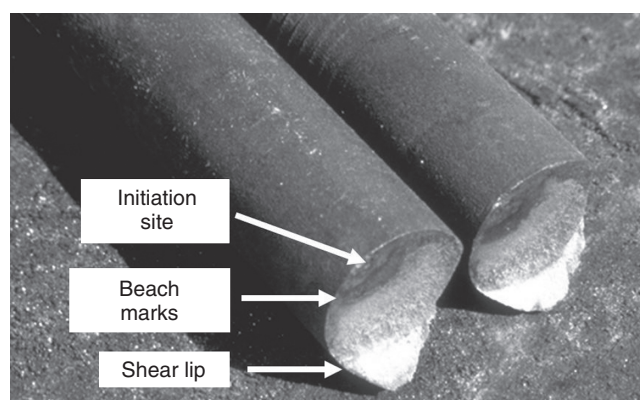
Design codes prior to the 1960s did not require toughness testing for equipment unless the equipment was to be operated below  $-20^{\circ}\text{F}$  ( $-29^{\circ}\text{C}$ ). Thus, older equipment may be susceptible to unexpected brittle fracture. This is a concern for any equipment, especially gas pipelines that may undergo rapid cooling due to Joule-Thompson expansive cooling. Rapidly expanding gas can cause the pipeline to become brittle and lead to brittle crack propagation in the pipeline.<sup>27</sup> The requirement for toughness testing was added to API Specification 5L for line pipe in 2000, and many gas pipelines constructed prior to this time may be subject to unexpected brittle behavior.

**Fatigue** Fatigue fracture is the failure of metal or equipment due to repeated loading and stress cycles. Figure 4.16 shows a typical fatigue curve for carbon steel, which is assumed to have an endurance, or fatigue, limit, below which failure will not occur even after many loading cycles. The endurance limit is an important concept in the designs of sucker rod strings, other pump components, and rotating equipment.

Fatigue crack initiation sites are usually surface flaws that act as stress risers that concentrate or magnify the applied stress. These can be corrosion pits on offshore structures, tong marks on drill pipe, machining grooves, or metallurgical defects. Once the crack starts to grow, the surface will frequently have concentric markings on the surface known as clam-shell marks or beach marks. These concentric half-oval marks are the result of



**Figure 4.16** Fatigue curve showing endurance limit.

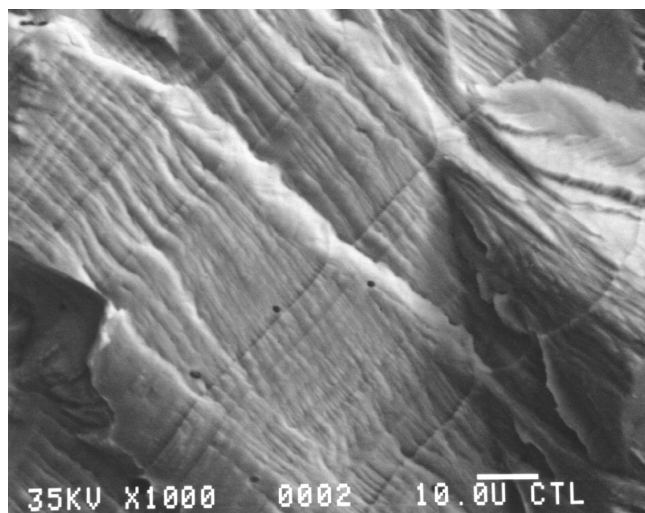


**Figure 4.17** Fatigue fracture in a sucker rod.

differential weathering as the crack progresses. Once the crack progresses to a certain level, the stresses are too high and the part fails by normal overload. This is shown in Figure 4.17, where the final failure produced shear lips as the sucker rod pulled apart by tensile overload.

Fatigue fracture surfaces will often produce a pattern showing individual crack propagation markings, called striations. This is shown in Figure 4.18, where the striations progress from the lower left to the upper right. These striations can only be seen at very high magnifications using electron microscopes. The spacing between striations is so small that they can only be seen using electron microscopes at very high magnifications.

Most fatigue failures can be classified as due to high-cycle fatigue, where failure, if it occurs, is after  $10^6$  cycles or more. Some oilfield equipment, for example, coiled tubing used for downhole inspections, is considered to be subject to low-cycle fatigue, which can occur after many fewer cycles, usually in the hundreds or less. Low-cycle fatigue is due to loading beyond the yield stress, whereas high-cycle fatigue is due to loading below the yield stress.



**Figure 4.18** Striations caused by fatigue. The horizontal magnification is 1000 $\times$ . Photo courtesy of Corrosion Testing Laboratories, Inc.

It is important to remember that submicroscopic defects, undetectable by modern inspection techniques, lead to eventual crack growth and propagation into fatigue failures. Even if no cracking is observed, it does not mean that the material has not been damaged by repeated loading cycles. This is the reason why drill pipe, coiled tubing for downhole inspections, and wireline is retired after too many “trips” or uses downhole.

**Stress Risers** Modern engineering practice has come to recognize that sharp defects, present in welds, fatigue cracks, corrosion pits, machined notches in fasteners, etc., can raise the effective stress level above the stress that would be calculated using a simple load per cross-sectional area calculation.

The recognition of this problem has led to the development of the field of engineering known as fracture mechanics. Modern computer programs using numerical techniques (finite element analysis, boundary integral analysis, etc.) enable engineers to predict the effect of defects of different sizes and geometries on the strength of various structures.<sup>4</sup> The effects of various stress risers on oilfield structures has been recognized for decades, and several commercial software packages are in widespread use in oilfield applications.<sup>26,28–35</sup>

## Creep

Creep is the time-dependent permanent (plastic) deformation of a material due to loading below the yield stress. In metals it is caused by atomic diffusion parallel to the stress axis. It is usually considered a high-

temperature problem ( $T > 0.4$  of the absolute melting temperature) and not a problem in upstream operations, but creep can cause elongation and bending in large continuous structures, for example, tubing in deviated deep wells.

Creep in polymers can occur at much lower temperatures and can cause shorting of electrical insulators and other isolated problems.

## Thermal Expansion

Thermal expansion and contraction can cause numerous problems in oilfield equipment. A major problem is the stresses resulting from welding. Other problems occur in heat exchangers, where thermal fatigue cracking can occur. This has been a recent problem in brazed aluminum heat exchangers and fusion-bonded (sintered) heat exchangers. Manufacturers of this equipment claim to have solved these problems, primarily by reducing the sharp geometries that led to stress intensity magnification.

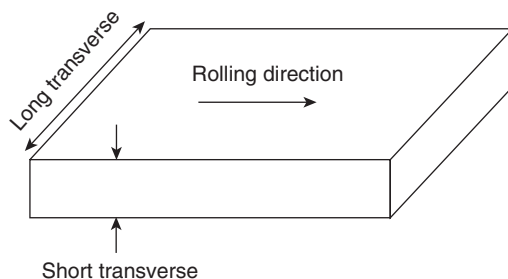
## FORMING METHODS

Oilfield metals and equipment can be fabricated and formed in a number of ways. It is important to understand how a metal was manufactured, because the metal, and objects made from metal, have different properties depending on how they were manufactured and assembled.

Once liquid metal is solidified, it can be used as a casting or it can be further shaped by a number of forming operations: forging, rolling, extrusion, or drawing. Each of these forming processes is most appropriate for different products, but they all have a number of characteristics in common.

## Wrought versus Cast Structures

All wrought (deformed after solidification) metals have crystal structures that reflect their forming process. Rolled plate, which is used to manufacture large-diameter pipe and process equipment, will have different crystal structures and different mechanical properties in all of the three principal directions shown in Figure 4.19. The same principles apply to wrought products formed by forging, drawing, and extrusion. This directionality does not only apply to mechanical properties. The corrosion resistance of metals will be different depending on the orientation of the exposed surface to forming directions. For rolled products, to include pipelines made from rolled plate, the most corrosion-susceptible direction is the short transverse direction.



**Figure 4.19** Principal directions of rolled plate.

This is because there are more grain boundaries exposed on these surfaces.

Defects in castings include inclusions, impurities from the melted metal or from the mold, and porosity due to entrained gases in the liquid metal. Wrought products are formed from castings and will have the same chemical composition and defect inclusions as the castings from which they are formed. The inclusions are generally ceramic materials due to material impurities or from the mold. The forming process breaks these inclusions, which tend to be very brittle, and spreads them out parallel to the primary forming direction. Metal crystals in wrought products are usually microscopic, whereas many crystals in castings can be large enough to be seen on polished surfaces with the naked eye. Grain boundaries in metals are a primary source of strengthening, so wrought products, with much finer grain sizes, tend to be stronger and more ductile than castings. Any porosity in the cast metal is likely to have been removed by the compression of the forming process. For all of these reasons, wrought metal products are stronger and are more reliable than castings.

## Welding

Welding is the preferred joining method for most oil-field piping systems and process equipment. With most welding processes, some of the metal is heated beyond the melting point while some of the structure is not heated at all. In between these two extremes is a wide variety of temperatures and times at different temperatures. This produces at least three distinct regions in the metallic structure:

**Weld Bead or Fusion Zone** This is a combination of filler metal and melted metal from the base metal being joined. It solidifies as a casting with the problems of castings plus added stresses due to the thermal contraction caused by solidification and cooling to the ambient temperature at different rates than the surrounding metal.

**Heat-Affected Zone (HAZ)** This is a region where the base metal has been affected by the heating associated with the weld. Phase changes in the metal can occur and produce different microstructures than the weld bead and the base metal. The results can be differences in mechanical and corrosion resistance properties.

**Base Metal** This is a metal that has not been heated enough to alter the metallic structure or corrosion resistance.

The three different heat-related regions are shown in Figure 4.20, and some of the defects associated with welds are shown in Figure 4.21.

Common defects associated with welding include:

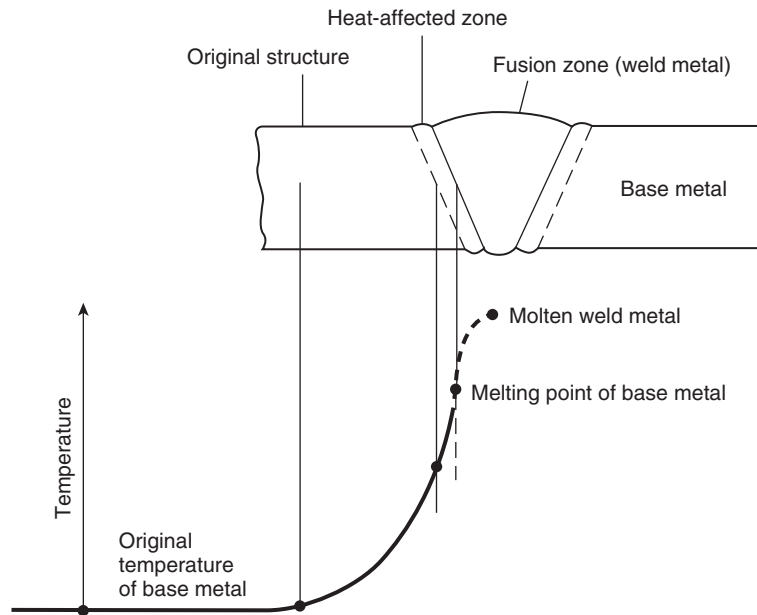
**Porosity** Internal porosity can be caused by trapped gases that have inadequate time to escape from the weld pool prior to solidification. Porosity is the cause of approximately 50% of all weld repairs.<sup>27</sup> Porosity can also be a problem in cast objects, but these objects are usually thicker than many welded structures and are less subject to the loss of strength associated with porosity.

**Cold Cracking** Hydrogen cracking is the principal cause of this problem. Quick cooling prevents the escape of hydrogen from the weld pool before solidification. Trapped hydrogen can cause hydrogen embrittlement and a variety of other problems that are discussed in detail under the heading Environmentally Induced Cracking in Chapter 5, Forms of Corrosion. Cold cracking is controlled by keeping filler metal electrodes dry and by avoiding hydrocarbon contamination of filler metal surfaces.

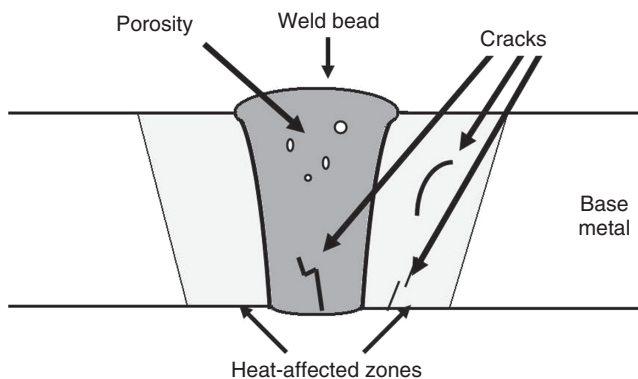
**Hot Cracking** This is also called sulfur cracking. It is restricted to low-grade carbon steel and some forgings with appreciable sulfur contents. Iron sulfides have low melting points and usually concentrate near the center of weld beads, where the metal solidifies last. Sulfide inclusions are weak and produce cracks as the weld cools.

**Slag Inclusions** This is usually due to poor welding procedures, including inadequate cleaning of surfaces before welding.

**Lack of Fusion** Sharp cracks form where the weld bead does not bond to the base metal. This may be due to inadequate surface cleaning prior to welding or due to insufficient shielding gas allowing a surface oxide to form on the weld bead. A lack of fusion usually produces sharp, crack-like defects.



**Figure 4.20** Temperature plot and associated regions associated with oxyfuel and arc welding.<sup>36</sup>



**Figure 4.21** Defects associated with welding.

**Incomplete Penetration** When the root pass (first pass) weld bead leaves crevices where the molten metal has not penetrated, this produces relatively sharp defects that may be detectable by radiography. Unlike porosity, these relatively sharp defects must be analyzed using a fracture mechanics approach.<sup>27</sup>

**Hard Spots** These are the result of rapid cooling that causes steel to transform from high-temperature austenite to either bainite or martensite upon uncontrolled cooling. Most authorities claim that welding-related hard spots produce martensite by uncontrolled quick cooling from high-temperature austenite to the martensite stability temperature (approximately 250–400°C [400–750°F] depending on alloy content).

**Striking Marks** These are the result of welding electrodes touching the metal surface and causing a spark. The heat generated by the strike can produce “hard spots” which can lead to subsequent cracking.

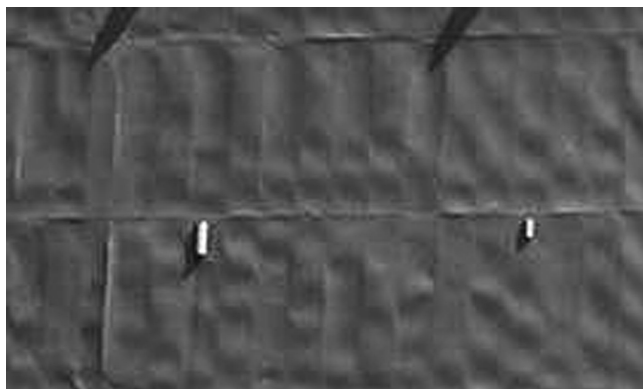
**Other Possible Causes of Cracks** A partial list of other causes of cracking includes movement before the weld sets, excessive delay between weld passes leading to internal hard spots caused by excessive cooling rates, and lamellar tearing due to inadequate inspection for laminations before starting the weld process.

**Distortion of Welded Structures** The above listing shows relatively small defects associated with the welding process. Stresses caused by shrinkage of high-temperature welds adjacent to relatively low-temperature base metal can also cause distortions on pipelines, tank walls and floors, and other structures. This is shown in Figure 4.22, which shows weld-shrinkage distortion on the side of a floating vessel. Similar distortions on the bottom of large storage tanks can lead to areas where water collects, is prevented from draining, and leads to corrosion.

Post-weld heat treating is sometimes specified to restore mechanical properties, reduce hardness and susceptibility to embrittlement, and relieve residual stresses. This adds to the cost, especially for field welds in piping systems.

**Weld Inspection** The following inspection methods are routinely specified for weld inspection:





**Figure 4.22** Distortion of exterior plates due to weld shrinkage.

**Radiography** This technique is mostly used to detect porosity, the problem associated with approximately 50% of all weld defect repairs. It can also detect incomplete penetration.

**Ultrasonics** This is another technique that is largely associated with detecting porosity. It can be automated and rapid, but usually does not leave the visual images provided by radiography. Ultrasonics can identify the depth of porosity, whereas radiography can only locate the defects in two dimensions.

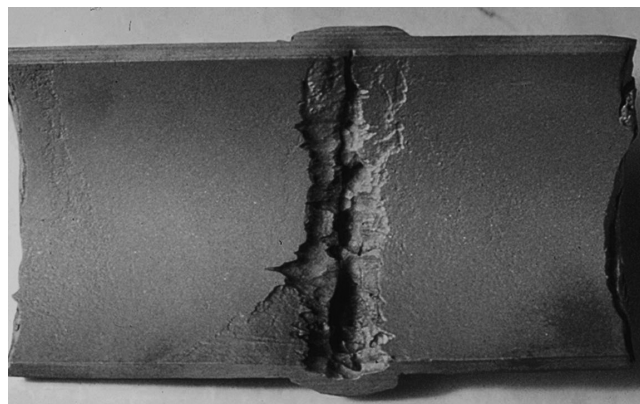
**Surface detection of cracks** Both radiography and ultrasonics are primarily useful in detecting porosity. Crack-like defects, if they reach or approach the surface, are detected by magnetic particle and dye penetrant inspection.

### ***Welding-Related Corrosion and Fracture Control***

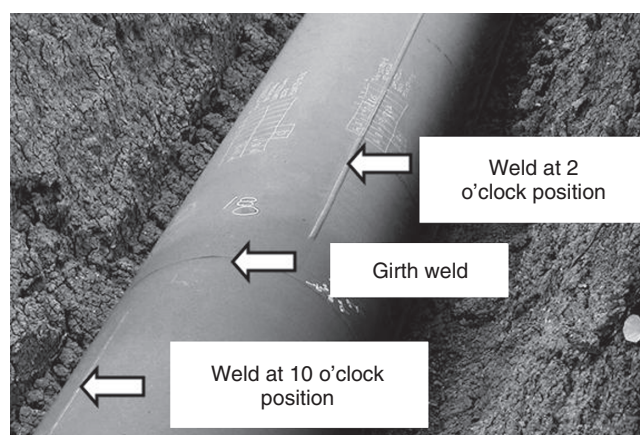
Preferential weld corrosion can be caused by the differences in microstructure between weld beads, HAZs, and base metals. This is minimized by filler metal chemistry specifications, which call for the filler metals to be cathodic to the base metals being joined. The small galvanic effect making the weld bead cathodic to the base metal is often achieved by the same alloying additions that are used to strengthen welds. Figure 4.23 shows an extreme case of corrosion caused by improper welding.

In-service repairs of piping and other equipment pose special problems not associated with welding for new construction. High cooling rates can be caused by liquid on the other side of the repair weld, and this can cause unwanted hard spots and cracking.<sup>27</sup>

The possibility of defects in welds is much higher than in wrought metal, for example, the plate from which welded pipelines are assembled. These welds can



**Figure 4.23** Weld line corrosion.<sup>37</sup> Photo courtesy NACE International, reproduced with permission.



**Figure 4.24** Pipeline with alternating longitudinal welds at 10 o'clock and 2 o'clock.

also be locations where slightly different microstructures lead to corrosion, either in the weld bead or in the HAZ. For these reasons, it is common to specify that longitudinally welded pipe joints be placed in pipelines with their longitudinal welds alternating at the 10 o'clock and 2 o'clock positions. This puts the welds in the upper quadrant of the pipeline, where corrosion is least likely to occur, and it decreases the chance that a rupture that may be associated with one longitudinal weld will run beyond the girth weld and into the next joint. This construction practice is shown in Figure 4.24.

Corrosion can also be concentrated at welds due to their rougher surfaces compared to the nearby metal. Roughness leads to increases in fluid turbulence, scale imperfections, and microbially influenced corrosion.

## MATERIALS SPECIFICATIONS

There are many organizations that issue materials standards used in the oil field. This section explains some of the organizations that issue standards or specifications followed by the worldwide industry. It is not comprehensive, and many other standards are also used. The relatively recent development of the Universal Numbering System (UNS) for Metals and Alloys has helped designers and purchasing organizations to compare various alloys. Most international suppliers of oilfield equipment and supplies can identify which standards their equipment or supplies will meet.

### API

API standards tend to be performance standards, in other words the manufacturer is given wide leeway on how to produce the intended product. The most commonly used oilfield materials standards are for OCTGs. At one time, these products were described in one API standard, API 5, but in recent years this has been subdivided into API 5D for drill pipe, API 5CT for casing and tubing, and API 5L for linepipe.<sup>5,16,38</sup>

A typical API specification will require well-defined strength levels and also specify mandatory limits on impact resistance, on carbon equivalents for weldability, and on a large number of other mechanical property and dimension requirements. The chemistry specifications will not translate to other common alloy designation systems, such as the UNS.

### AISI—The American Iron and Steel Institute

AISI steel specifications refer to chemical composition ranges and limits on steels, in the same way as SAE (formerly the Society of Automotive Engineers) steel designations, and they are often stated together, for example, AISI/SAE 4340.

### ASTM International—formerly the American Society for Testing and Materials

ASTM has a long history of supplying alloy designation standards. Metal standards are listed by the sponsoring committee.

Standards starting with the letter A pertain to ferrous metals, for example, A36—Carbon Structural Steel, and ASTM A353—Pressure Vessel Plates, 9 Percent Nickel, Double-Normalized, and Tempered.

Standards starting with the letter B pertain to non-ferrous metals, for example, B209—Aluminum and Aluminum Alloys, and B337—Titanium and Titanium Alloy Pipe.

Other letters are used for nonmetallic materials, test methods, etc.

In addition to ASTM standards for alloys, ASTM has cooperated with other organizations to develop a UNS described in ASTM E527—Numbering Metals and Alloys in the Universal Numbering System.<sup>39</sup>

### ASME

ASME Materials Specifications are derived from ASTM standards and have an additional S in the prefix. As an example, ASTM A106 becomes ASTM A106/ASME SA 106—Seamless Carbon Steel Pipe for High Temperature Service.

Most pressure vessel design is covered by international codes, the most common of which are ASME B31.3—Process Piping and the ASME Boiler and Pressure Vessel Code Sections. In general, only materials recognized by ASME can be used in these designs. Because ASTM has jointly developed the UNS with SAE (see below), it is possible that metals produced to other standards can be cross-referenced to become acceptable for ASME design codes.

### SAE International

For many years, SAE standards were usually listed as AISI/SAE standards, but in recent years, the practice has been discontinued, because AISI does not issue chemical requirement specifications. Common SAE chemistry designations are listed in Table 4.3. The first two numbers indicate the alloy grouping, and the last two digits list the nominal percentage carbon expressed in 0.01% increments; for example, 1040, 4140, and 4340 alloys all have 0.40% C as indicated by the last two digits of the alloy designation.

**TABLE 4.3 SAE Carbon and Alloy Steel Grades Used in Oilfield Equipment**

SAE Designation	Type
Carbon steels	
10xx	Plain carbon steel (Mn 1.00% max)
15xx	Plain carbon steel (Mn 1.00 to 1.65%)
Manganese steels	
13xx	Mn 1.75%
Chromium-molybdenum (Chromoly) steels	
41xx	Cr 0.5–0.8%, Cr 0.5%, Mo 0.12–0.30%
Nickel-chromium-molybdenum steels	
43xx	Ni 1.8%, Cr 0.5%, Mo 0.25%

**TABLE 4.4 UNS Numbering for Alloys**

Designation	Alloy System
Axxxxx	Aluminum alloys
Cxxxxx	Copper alloys, including brass and bronze
Fxxxxx	Cast iron
Gxxxxx	Carbon and alloy steels
Hxxxxx	Steels—AISI H steels
Jxxxxx	Steels—cast
Kxxxxx	Steels, including maraging, stainless steel, HSLA, iron-base superalloys
M1xxxx	Magnesium alloys
Nxxxxx	Nickel alloys
Rxxxxx	Refractory alloys
R03xxx	Molybdenum ALLOYS
R04xxx	Niobium (columbium) alloys
R05xxx	Tantalum alloys
R3xxxx	Cobalt alloys
R5xxxx	Titanium alloys
R6xxxx	Zirconium Alloys
Sxxxxx	Stainless steels, including precipitation hardening stainless steel and iron-based superalloys
Txxxxx	Tool steels
Zxxxxx	Zinc alloys

## UNS

Many different standards exist for materials, and the UNS for Metals and Alloys is a joint effort by ASTM and SAE to list metals in a uniform manner instead of using proprietary or local standard designations. UNS designations are not specifications, because they establish no requirements for form, condition, property, or quality. UNS numbers are identifiers of a metal or alloy having controlling limits in specifications published by some other standards organization. Whenever possible, identification numbers from existing systems were incorporated into UNS designations; for example, AISI/SAE 304 stainless steel is UNS S30400.<sup>39–41</sup>

API specifications are performance specifications and frequently do not have controlling limits, for example, on chemistry. For this reason, API materials, for example, 5L line pipe, do not have UNS numbers. They can be manufactured from a variety of UNS-designated alloys (Table 4.4).

## NACE—The Corrosion Society

NACE does not classify alloys, but MR0175/ISO15156 is a commonly used guideline into oilfield alloy selection. This standard, and all recent NACE publications, refers to alloys by UNS number whenever such numbers are available. The alloys discussed in various parts of the standard are:<sup>11,12</sup>

- Carbon steels and cast irons
- Austenitic stainless steels
- Highly alloyed austenitic stainless steels
- Solid-solution nickel-based alloys
- Martensitic stainless steels
- Duplex stainless steels
- Precipitation-hardened stainless steels
- Precipitation-hardened nickel-based alloys
- Cobalt-based alloys
- Titanium and tantalum
- Copper and aluminum

## Other Organizations

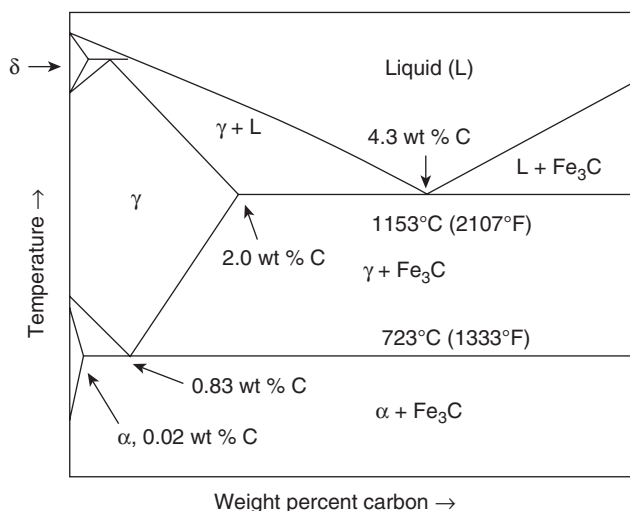
The International Standards Organization, American National Standards Institute, det Norske Veritas, and other organizations supply standards for materials. In many cases recent standards have reflected efforts to make existing standards compliant with the larger, non-materials organizations' standards; for example, 2009 API 5L for line pipe became ANSI/API 5L—Specification for Line Pipe.

## Use of Materials Specifications

This book has been careful to avoid listing specifications and standards by specific date, and new equipment should be specified according to current versions of applicable codes and standards. Codes and standards are written based on the best available information at the time of writing, and they are updated. When specifying a standard in design or purchasing documents, it is not appropriate to use a general statement referring to “the latest version” of a code or standard. The specific edition of the standard in question should be clearly stated in the specification or purchasing document to avoid any disputes after the order is placed.<sup>42</sup>

As materials producers have improved process control and reduced inventories in recent years, it has become common for some suppliers to offer equipment or supplies that will exceed the specified mechanical properties of a given alloy. Unfortunately, stronger materials are frequently brittle, and the user must be sure to specify unacceptable maximum mechanical properties in addition to the commonly specified minimums. Some materials standards do not have specified maximum properties. Even when standards, for example, the API 5L line pipe standard, have clearly stated maximums, it is common for suppliers to offer stronger materials if the specified material is not in stock. This concern with exceeding maximum properties is especially important for any application where





**Figure 4.25** The iron-iron carbide phase diagram.

embrittlement due to cold temperatures or  $H_2S$  is likely to be encountered.<sup>27</sup>

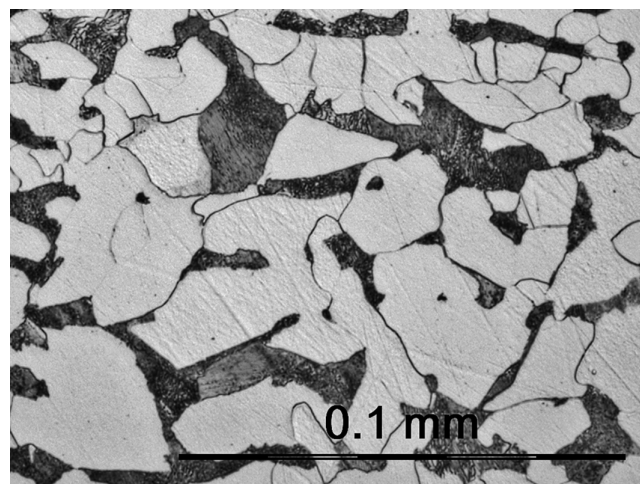
For large projects, for example, subsea pipelines, it is important to collect the statistical distribution data on the delivered material properties and retain it in a central location. Once the project is finished, it is difficult to obtain this information if it is necessary due to any one of a number of circumstances.<sup>27</sup>

### CARBON STEELS, CAST IRONS, AND LOW-ALLOY STEELS

Carbon steel is the most commonly used metal in the oil field. Depending on the chemistry, primarily carbon content, and the heat treatment history, carbon steel can vary in yield strength from about 250 mPa (36 ksi) for structural steel to over 1380 Mpa (200 ksi) for wire line. Most carbon steel used in the oil field is specified based on yield strength, and yield strengths of over 690 mPa (100 ksi) are common for many OCTG steels. Cast iron is much less commonly used in oilfield applications.

Figure 4.25 is the iron-iron carbide phase diagram showing the phases that form in iron-carbon alloys used for making steel and cast irons. Steels can have up to 2% carbon, but most oilfield alloys have only a small fraction of that, up to 0.4% in the case of drill pipe and other high-strength applications, but much lower for most other applications. Cast irons have 2% carbon or more, which makes them less expensive due to their lower melting points, but they are so brittle that their applications in the oil field are very limited.

The diagram shows that  $\alpha$ -ferrite has a maximum carbon content of only 0.02% at 723°C (1333°F). This



**Figure 4.26** Microstructure of a typical carbon steel. Photo courtesy of J. Ribble, Materials Evaluation & Technology Corporation, <http://www.metco-ndt.com>.

means that carbon steel at room temperature will consist of a mixture of essentially pure  $\alpha$ -ferrite and a compound ceramic material,  $Fe_3C$ , known as cementite. This two-phase structure serves to greatly strengthen carbon steel, which is much stronger than pure iron.

Figure 4.26 shows a typical microstructure for carbon steel. The light areas are  $\alpha$ -ferrite, almost pure iron. The dark areas are alternating bands of  $\alpha$ -ferrite and cementite, iron carbide  $Fe_3C$ . These alternating bands are a composite structure known as pearlite. Approximately 25% of the surface area shown in this picture is pearlite, indicating that the carbon steel had approximately 0.2% carbon. Most carbon steels used in oilfield applications will have similar microstructures and carbon contents.

The following phases are commonly found in carbon steels:

**$\alpha$ -Ferrite:** This phase, which is usually called ferrite, is the BCC form of iron thermodynamically stable at room temperature. It is reasonably ductile and can be work-hardened by low-temperature plastic deformation.

**Cementite:** Cementite is a complex ceramic material having the approximate composition  $Fe_3C$ . Cementite was named by early metallographers who noted how hard it is. Any plastic deformation in the ferrite phase tends to be stopped when it reaches a cementite grain boundary, and the hardness of cementite accounts for the strength of carbon steels.

**Austenite:** Above 723°C (1333°F) carbon steel starts to form the  $\gamma$  phase of iron called austenite. This phase is FCC, very ductile, and relatively soft. All

of the carbon in carbon steels is also soluble in austenite, and this is very useful, because it makes hot steel ductile and amenable to forging, rolling, and other forming methods even in relatively thick sections.

**Pearlite:** The microscopes available to nineteenth-century steel researchers did not show the alternating plates of ferrite and cementite shown in Figure 4.24. They named the grey areas on the steel surface pearlite thinking it was a separate phase. Pearlite forms at the austenite grain boundaries as steel is cooled from higher temperatures. There is insufficient energy to allow diffusion into separated ferrite and cementite phases, so the alternating plate structure forms from the last austenite to transform. The composition of pearlite is 88% ferrite and 12% cementite.

**Martensite:** Martensite is a body-centered tetragonal form of iron that forms at lower temperatures (approximately 250°C–480°F) from austenite that has not transformed into ferrite at higher temperatures during the cooling process. It is considered undesirable in pipeline steels and many other oilfield structures. The section on Heat Treatment of Carbon Steels discusses this in greater detail.

**$\delta$ -Ferrite:** The first solid metal to solidify from liquid steel has a BCC crystal structure. It is called ferrite, because it has the same high-iron crystal structure as low-temperature  $\alpha$ -ferrite. The presence of  $\delta$ -ferrites is generally considered to be undesirable and an indication of improper heat treatment or welding.

Spheroidized and bainitic steels are specialized terms applied to carbon steel to indicate the shape of the cementite in the two-phase structure. They are generally not important in oilfield steels.

### Classifications of Carbon Steel

The most common uses for carbon steel are for structures, OCTGs, and piping and process equipment. The term “carbon steel” is applied to any alloy consisting of iron plus carbon. Other elements may be added for deoxidation or machinability purposes. The term “killed steel” is applied to steels where the dissolved gases have been removed by the addition of either silicon or aluminum. It is common to have minimum residual content requirements for these elements to insure that most of the dissolved gases have been removed. Most carbon steels used in the oil field are killed steels.

**Low-Carbon Steels** These steels can contain up to 0.30% C. Line pipe, tubing, and casing are usually made from low-carbon steels.<sup>4,5,16,38</sup>

**Medium-Carbon Steels** Medium carbon steels have carbon contents from 0.30% C to 0.60% C and have increasing manganese contents intended to minimize the effects of impurities such as sulfur. The somewhat higher carbon content allows them to be heat-treated and used in the quenched and tempered condition.

**High-Carbon Steels** These steels have from 0.60% C to 1.00% C and from 0.30% Mn to 0.90% Mn. They can be hardened by the quenching and tempering process and are very strong and hard. Their primary applications are for relatively small equipment needing maximum hardness. They are seldom specified for oil-field applications because of their brittle behavior. One notable exception is springs for control devices, although these are usually made from alloys other than carbon steel.

**High-Strength Low-Alloy (HSLA) Steels** These are also called microalloyed steels and have from ~0.25% C to 0.50% C and Mn contents up to 2.0%. Small quantities of chromium, nickel, molybdenum, copper, nitrogen, vanadium, titanium, and zirconium are added in various combinations.

**Carbon-Manganese Steel** The manganese content in carbon steels is sometimes increased for the purpose of increasing depth of hardening and improving strength and toughness. Carbon steels containing over 1.2% up to approximately 1.8% manganese are referred to as carbon-manganese steels. Some published books and standards discuss the use of carbon-manganese steels for pipelines,<sup>27,43</sup> but a review of the API 5L standard for line pipe steel shows only maximum manganese contents (from 0.60 to 1.85 depending on specified strength levels).<sup>38</sup> With no minimum standards for manganese, purchases according to API 5L must specify the manganese level if it is desired. NACE RP0175/AISI15156-2 for carbon and low-alloy steels in H<sub>2</sub>S service recognizes carbon-manganese steels for downhole service.<sup>11</sup>

**Low-Alloy Steel** A common definition of low-alloy steels is steels with total alloying additions of 8% or less. Examples of low-alloy steels are listed in Table 4.3. Most authorities consider them as alternatives to carbon steels, and they are usually chosen because of their improved mechanical properties. They are often cathodic to carbon steels, but they must be protected from corrosion in the same ways as carbon steels. The only exceptions to the previous sentence are weathering



steels, a form of structural steel intended for use in atmospheric exposure without protective coatings.

**High-Alloy Steel** These alloys have 8% or more alloying additions and are considered to be CRAs. The most common examples of high-alloy steels are stainless steels. It should be noted that the term “high-alloy steel” is not synonymous with “stainless steel,” because most authorities consider stainless steels to be ferrous alloys with a minimum of 11% or more chromium.

### Strengthening Methods for Carbon Steels

The following discussion covers the most common strengthening methods for carbon steels. Similar methods are applicable for some CRAs, but many CRAs cannot be strengthened by some of the methods applicable to carbon steels.

**Work Hardening** Ductile metals, including carbon steels, can be work-hardened by deformation. The only common use of this practice in oilfield applications is wire, for example, for downhole wireline applications. It is not practical to work-harden plate and similar thick shapes due to the excessive pressures necessary to do so.

**Alloying** The most important alloying addition for carbon steels is carbon. Unfortunately, brittleness can result in high-carbon steels, so oilfield alloys typically have approximately 0.2% for most applications and approximately 0.4% for drill pipe, erosion-resistant wellhead equipment, and other high-hardness applications. The strengthening effects of carbon additions are limited by metal thickness, which slows cooling and limits this kind of hardening in thicker structures. Common alloying additions for through-thickness hardening include the chromium-molybdenum (chromoly) and nickel-chromium-molybdenum alloys shown in Table 4.3. This is discussed further in the section on Heat Treatment of Carbon Steels.

**Grain Size Refinement** Small-grained alloys are stronger than larger-grained alloys having the same chemistry. Steels can be specified for fine-grained practice, which may cost an additional 10–40% for typical carbon steel OCTGs. Steelmakers add nucleation agents such as aluminum to insure that desired small-grain products are produced with practical cooling rates. It is common to normalize steel after solidification to further refine the grain size. Normalization can also be used on conventional steels and will have grain-size refinement effects, though not as much as with deliberately microalloyed steels.

**Second-Phase Hardening** All carbon steels have multiple phases. Carbon is insoluble in low-temperature  $\alpha$ -ferrite, and the presence of cementite in various forms is the primary strengthening mechanism for most oilfield carbon steels.

### Heat Treatment of Carbon Steels

The iron–iron carbide phase diagram, Figure 4.25, is an equilibrium diagram. It shows the phases that will be present if the metal is exposed for relatively long times at the indicated temperatures. Quick cooling, or quenching, can result in residual high-temperature phases at lower temperatures. This is why welding with insufficient preheating of the adjacent parent metal can produce  $\delta$ -ferrites in the weld bead even though most of the metal has a different microstructure.

Most oilfield steel is too thick to be cold-worked, so it is common that the final shape of a forging or the final thickness of plate to be formed into line pipe or process equipment was accomplished while the steel was at elevated temperatures in the relatively ductile austenite condition. Cooling from this temperature can produce different microstructures and properties depending on the cooling rate. The centers of thick sections will cool at slower rates and have different microstructures.

The following terms are commonly used in heat treating of steels:

**Annealing** This is a general metallurgical term for a heating process used to soften a metal. In steels, it often refers to slow cooling from the austenite temperature region, but stress-relief annealing at lower temperatures is also common, for example, in welded structures.

**Quenching** Quenching refers to the quick cooling of a metal. The rapid removal of energy from the metal tends to limit atomic diffusion and may “freeze in” a higher-temperature crystal structure.

**Tempering** Steels are tempered to remove unwanted martensite, a brittle metal phase formed by quickly quenching austenite so fast that the thermodynamically stable  $\alpha$ -ferrite plus cementite structure cannot form. This is discussed in detail in the sections on Quenching and Tempering.

**Normalizing** The “normal” way of cooling steel is to let it air cool. Some manufacturing processes, for example, welding or upsetting the heated end of a tube (done with the upset region at austenite-stable temperatures), produce different microstructures and different corrosion resistance in the fully heated region, in the HAZ near the hottest region, and in those sections of

the part that were not heated. The entire part is then reheated to form austenite and then allowed to air cool producing a uniform “normalized” microstructure throughout the entire part. This is called “full-length normalizing.”

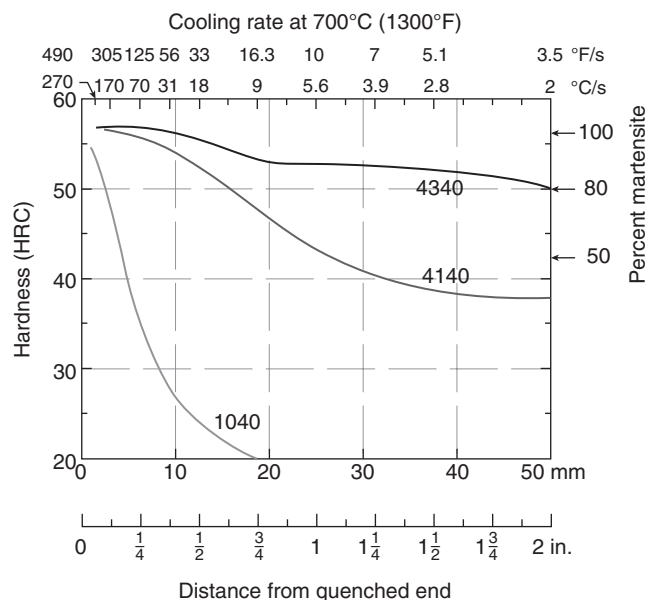
**Hardenability** The hardenability of steel is a measure of the hardness and the depth to which a steel may be hardened during quenching. Low-carbon steels lack insufficient carbon to be hardened. Medium- and high-carbon steels often have additional alloying additions to improve their hardenability.

### Quenched and Tempered (Q&T) Steels

Quenching is the quick cooling of a metal, usually to “freeze” in a high-temperature microstructure or to prevent transformation into an unwanted microstructure. It is applied to steels by first heating the steel to the austenite-stable region and converting all of the metal to a single-phased alloy with a uniform distribution of alloying and impurity elements. The steel is then quickly cooled to minimize the formation to  $\alpha$ -iron ferrite plus cementite. Metal that remains as austenite is then converted to martensite, a body-centered tetragonal crystal structure. This conversion to martensite starts at temperatures between 250°C and 350°C (440°F and 660°F) depending on alloy composition. The temperatures at which martensite forms are so low that diffusion of carbon to form cementite is practically nonexistent.<sup>3</sup>

Martensite is very hard and brittle and is, for all practical purposes, useless. The reason for this hardness is the fact that the carbon atoms, which were soluble in the high-temperature austenite, are trapped in interstitial sites in the martensite crystal. These trapped atoms are too big for the interstitial sites and put tremendous pressure on the surrounding iron atoms.

Quenched steels are then “tempered” by raising the metal to temperatures below the austenite transformation temperature and allowing the carbon to diffuse and form a fine-grained microstructure called “tempered martensite.” This tempered martensite is a mixture of  $\alpha$ -ferrite and cementite and, due to the fine-grained structure, it is much stronger and tougher than pearlitic steel formed by normalizing or other heat treatment processes. Because the quenching and tempering process involves removing energy for diffusion and phase transformation (quenching) and reintroducing energy (tempering), the final product frequently contains a mixture of retained austenite, untransformed martensite, and tempered martensite. The amount of each phase depends on the time at annealing temperature and the thickness of the metal in question.<sup>3</sup>



**Figure 4.27** Hardness after quenching for three different steels having the same (0.40%) carbon content.<sup>3</sup> Modified from figure 14.8, p. 580 in Callister and Renthwisch.

The elimination of brittle martensite during the tempering process brings back ductility lost due to quenching, and the very fine microstructure means that the steel is very strong. The final properties produced by the quenching and tempering process depend on the amount of carbon in the steel, so this process cannot be applied to low-carbon steels.

Alloying is used to increase the thick-section hardenability of steels. Figure 4.27 compares the hardenability of three steels, all of which have the same carbon content. Because they all have the same carbon content, they all form the same amount of martensite at the water-quenched surface, and the hardness is the same at the surface. As the distance from the water-quenched surface increases, the hardness of the plain carbon steel falls off quickly, while the other two alloys maintain hardness deeper into the alloy. The right-hand axis of this figure shows that this hardness is due to the higher percentages of martensite in the two alloy steels.

Q&T steels are used in many oilfield applications including drill pipe, wellhead equipment, and other equipment that must be very strong, hard, and ductile.

### Carbon Equivalents and Weldability

Weldability of carbon steel is affected by carbon content, which affects the brittleness and microstructure of the weld bead and the HAZ. Carbon equivalents, which account for the effect of alloying additions, are fre-

quently used in specifying acceptable alloying additions to metals that must be welded, for example, pipelines. There are a number of formulas for calculating carbon equivalents, but the formulas used in API 5L for pipeline steels are:<sup>38</sup>

$$CE(Pcm) = \frac{Si}{30} + \frac{Mn}{20} + \frac{Cu}{20} + \frac{Ni}{60} + \frac{Cr}{20} + \frac{Mo}{15} + \frac{V}{10} + 5B \quad (\text{Eq. 4.2})$$

This is used for steels with carbon contents less than or equal to 0.12% and

$$CE(IIW) = C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Ni + Cu}{15} \quad (\text{Eq. 4.3})$$

This is used when the carbon content is greater than 0.12%.

Maximum carbon equivalents are intended to avoid brittleness in welds and HAZs.

### Hard Spots

Welding can leave “hard spots” in carbon steel structures, such as pipelines. This is often caused by quickly cooling (quenching) steels from high temperatures to form martensite. If post-weld heat treatment is not practical, then the martensite remains in the metal and can become a potential source of problems. Brittle fractures, including those associated with H<sub>2</sub>S cracking, can result. The normal way to avoid this problem is to heat the surrounding metal prior to welding. This prevents the quick cooling which allows martensite to form. One of the purposes of carbon equivalents in metal specifications is to minimize the likelihood of hard spot formation.<sup>44</sup>

### Cleanliness of Steel

Steel purity strongly affects many properties. As steel first solidifies from the melt and is formed into plate or similar products, the cooling and forming processes tend to concentrate impurities, especially brittle inclusions like manganese sulfide stringers, near the center of the metal. When the steel is further processed by rolling or extrusion, these defects are flattened and spread out parallel to the forming direction. Large inclusions are most likely to be found near the center of plate or piping. These inclusions affect susceptibility to embrittlement and hydrogen blistering. They also affect toughness. This is why specifications for steel often require Charpy impact and tensile tests from mid-thickness locations.

**Oxygen** Steel is deoxidized while in the liquid state by the addition of silicon or aluminum which “kills” the steel. Calcium is also sometimes used for this purpose, especially in pipeline steels.<sup>27</sup> Semi-killed steels, for example, A53 pipe and A285 plate, have more oxide inclusions than fully killed A106 pipe and A516 plate.<sup>45–49</sup> These oxide inclusions lower notch toughness and other mechanical properties in the through-thickness (short transverse) direction.

**Sulfur** Sulfur affects the toughness of steels due to the presence of manganese sulfide stringers and other inclusions. The purity of steels has improved over recent decades. Sulfur levels in modern steels are often less than they were in the 1970s (less than 0.010% vs. 0.025% in the 1970s). This is one reason why modern pipeline steels are considered to be less susceptible to brittle behavior of all types.

### Cast Irons

Cast irons are alloys of iron and carbon having approximately 10 times the carbon content of typical carbon steels. This carbon is in the form of graphite flakes or nodules. The graphite is very weak, and this makes cast irons very brittle. They are seldom used on upstream oil and gas operations except for water service. Even in water service, it is common to use cast steel for critical applications like fire water.

Any component available in cast iron can be made from cast steel but usually with a cost penalty. Most upstream operators consider the increased reliability more important than the small cost penalties.

### CRAS

NACE defines CRAs as alloys “... whose mass-loss rate in produced fluids is at least an order of magnitude less than that of carbon and low-alloy steel, thus providing an alternative method to using inhibition for corrosion control.”<sup>50</sup> There are a wide variety of CRAs and a number of different ways they can be classified. This section discusses the following alloy groups:

- Iron-nickel alloys
- Stainless steels
- Nickel-based alloys
- Cobalt-based alloys
- Titanium
- Copper
- Aluminum

### Iron-Nickel Alloys

These alloys are more corrosion resistant than carbon steels, but their relative ductility at low temperatures is the more important reason for their use in oilfield applications.

Iron-nickel alloys are used for above-ground cryogenic storage tanks for LNG, because these alloys have sufficient ductility at LNG temperatures ( $-162^{\circ}\text{C}$  [ $-260^{\circ}\text{F}$ ]). The addition of nickel to iron results in alloys where the transition of high-temperature austenite to  $\alpha$ -ferrite is retarded. Alloys having 5–10% nickel will have a mixture of high-iron  $\alpha$ -ferrite, which is subject to embrittlement at low temperatures, and austenite, which is ductile at the temperatures found in LNG storage and similar applications. The dual-phased structure still has ferrite, but the resulting alloy is ductile enough for static structures like storage tanks.

LNG storage tank walls are typically constructed from welded iron-nickel alloys (9% nickel alloys are most commonly used),<sup>51–54</sup> with piping and similar attachments made from austenitic stainless steel, which is more expensive, but has better resistance to thermal fatigue. Welds on these LNG tanks use nickel-based alloys.<sup>55,56</sup> Corrosion is not a problem at cryogenic temperatures, so galvanic coupling between nickel steel and stainless steel is not a problem.

Austenitic stainless steel and aluminum alloys are also ductile at LNG temperatures, and they are sometimes used for building smaller storage tanks, but large containment vessels are usually welded from iron-9 nickel because of expense considerations. This technology has been in use since the 1940s and is well-established worldwide.

### Stainless Steels

Stainless steels are usually defined as alloys having a minimum of 11% chromium in addition to other alloying additions.<sup>57</sup> The names attached to the various classes of stainless steels usually derive from the predominant crystal structure that determines their mechanical properties. Stainless steels can have a wide variety of mechanical properties, but the reason for using them is for corrosion resistance, and this will be emphasized in the following discussions.

The commonly recognized classes of stainless steels are:

- Martensitic stainless steels
- Ferritic stainless steels
- Austenitic stainless steels
- Duplex stainless steels
- Precipitation-hardening stainless steels

**Martensitic Stainless Steels** Martensitic stainless steels are used in upstream production and pipelines more than any other class of CRAs.<sup>58–61</sup> There are two reasons for this: the martensitic structure produces strong, tough alloys and, compared with other stainless steels, the martensitic alloys have the lowest alloying content and are thus less expensive. They can also be heat-treated to approximately the same strengths as carbon steel tubular goods.

Martensite is produced when high-temperature austenite is oil-quenched to martensite transformation temperatures, between  $250^{\circ}\text{C}$  and  $350^{\circ}\text{C}$  ( $440^{\circ}\text{F}$  and  $660^{\circ}\text{F}$ ) depending on alloy composition. The alloys are then tempered to improve toughness. API casing, tubing, and line pipe specifications identify two different chromium contents for iron-chromium alloys—9% and 13% chrome. The 9% chrome has insufficient alloying to be a true stainless steel and is seldom specified. The use of 13% chrome alloys has increased in recent years due to increased production in more aggressive environments and concerns that the cost of corrosion monitoring, corrosion inhibitors, repairs and, most importantly, lost production, outweigh the added cost of CRAs. As one example, the materials cost of a carbon steel subsea pipeline, including both metal acquisition and welding, is approximately 25% of the total cost. Changing to CRAs doubles the materials cost, but it only increases the total initial cost of the pipeline by approximately 25%. Many operators consider this additional initial cost justified.

Martensitic stainless steel tubular goods are usually specified using API specifications, while other industrial specifications based on UNS or other international standards are common for other applications.<sup>58</sup> Table 4.5 shows some of the most commonly used martensitic stainless steels used in oil and gas production.

The limited alloying content of martensitic stainless steels means that while they are more corrosion resistant than carbon steels, they cannot withstand aggressive environments. They are mostly used in applications where  $\text{CO}_2$  corrosion is a problem and  $\text{H}_2\text{S}$ , if present, is at relatively low concentrations. NACE RP0175/ISO15156 places limits on the hardness that these alloys can have in  $\text{H}_2\text{S}$  service depending on alloy type and application.<sup>12</sup>

The amount of chromium that can be added to martensitic stainless steels is limited because austenite, which is necessary for heat treatment to produce martensite, does not form at chromium contents greater than 12–17% Cr. The upper limits are determined by other alloying additions, and the highest commercially available martensitic stainless steel routinely approved for  $\text{H}_2\text{S}$  service, UNS S42500, has 15% chrome.<sup>12</sup> Iron-chrome alloys with higher chrome contents have ferritic



**TABLE 4.5 Nominal Composition of Selected Martensitic Stainless Steels Used in Oil and Gas Production**

UNS Number	Name	C max	Fe	Cr	Ni	Mo	Other
S41000	410	0.15	bal	12.5			
S41425	Super 13Cr	0.05	bal	13.5	5.5	1.75	Cu 0.3
S41426	Super 13Cr	0.03	bal	12.5	5.5	2.25	Ti 0.01, V 0.5
S41427	Super 13Cr	0.03	bal	12.5	5.3	2	Ti 0.01, V 0.3
S42000	420	0.15	bal	13			
K90941	9Cr 1Mo	0.15	bal	9			
J91150	CA 15	0.15	bal	12.75			
	API L80-9Cr	0.15	bal	9	0.5 max	1	
	API L80-13Cr	0.15–0.22	bal	13	0.5 max		

**Figure 4.28** External corrosion of API 13Cr L80Cr tubing stored outdoors for several years.

microstructures and are discussed in the section on Ferritic Stainless Steels.

Storing API 13Cr tubulars is very important. Most 13Cr failures come from storage problems. Figure 4.28 shows 13Cr tubing that was stored outdoors for several years. Note how the exterior of the tubing has corroded, but the head has not. The reason the box end of the tubing has not corroded is because most 13Cr downhole tubing has couplings made of another alloy with a different hardness to avoid galling or seizing during makeup. The premium couplings are usually made from more CRAs.

The obvious corrosion shown in Figure 4.28 emphasizes that “stainless steel” is not immune to corrosion. Martensitic stainless steels have the lowest alloying contents of any CRAs, and they corrode, even in atmospheric corrosion. This corrosion susceptibility has led many organizations to develop storage guidelines for

CRA tubular goods, which are often stored in field locations for long periods before they are used.

Downhole OCTGs are the most common oilfield applications for martensitic stainless steels. Wellhead equipment is often made from cast or forged versions of these alloys. Surface applications beyond the wellhead are limited because oxygen ingress can cause severe pitting in these alloys. The use of martensitic stainless steels for internal corrosion control of subsea pipelines is increasing.<sup>27</sup>

**Ferritic Stainless Steels** Ferritic stainless steels find limited use in oilfield applications. They have higher chromium concentrations than martensitic stainless steels, but their limited strength due to the lack of tempered martensite makes them less desirable for many applications. Table 4.6 shows some ferritic stainless steels listed in NACE MR0175/ISO15156.<sup>12</sup>

**Austenitic Stainless Steels** Austenitic stainless steels are the most commonly used stainless steels on a worldwide basis. Their use in oilfield applications is limited by their strength and their susceptibility to pitting and stress corrosion cracking in chloride and other halide-containing environments. The maximum temperature limit for avoidance of stress corrosion cracking is widely assumed to be 60°C (140°F).

The austenitic structure (FCC) is very ductile, and these stainless steels can be drawn into very thin tubing. Cold-worked austenitic stainless steels are usually annealed to relieve residual stresses before use in corrosive environments.

Table 4.7 shows several austenitic stainless steels. Type 304 (UNS S30400) stainless is the most common form of stainless steel and is the basis for all of these alloys, which are often called “18-8” stainless steels, because their nominal composition is based on the original German stainless steel compositions having 18% chrome and 8% nickel.



**TABLE 4.6 Nominal Composition of Selected Ferritic Stainless Steels Approved for Use in H<sub>2</sub>S Oilfield Service**

UNS Number	Name	C max	Fe	Cr	Mo	Other
S40500	405 SS	0.08	bal	11.5 to 14.5		Al 0.10 to 0.30
S43000	430 SS	0.12	bal	16.0 to 18.0		
S44635	26-1 Cb	0.10	bal	25.0 to 27.0	0.75 to 2.50	Nb 0.05 to 0.20

**TABLE 4.7 Nominal Composition of Representative Austenitic Stainless Steels**

UNS Number	Name	C max	Cr	Ni	Mo	Other	Minimum PREN <sup>a</sup>
S30400	304SS	0.08	19	9.25			18
S30303	304L	0.03	19	9.25			17
S31600	316SS	0.08	17	12	2.5		23
S31603	316L SS	0.03	17	12	2.5		23
S31700	317 SS	0.08	19	13	3.5		28
S32100	321 SS	0.08	18	10.5		Ti <sub>min</sub> = 5xC	17
S34700	347 SS	0.08	18	11		Nb <sub>min</sub> = 10xC	17

<sup>a</sup> The compositions shown in this table are the averages between the minimum and maximum levels. PREN numbers are calculated based on minimum numbers.

Unfortunately, 304 stainless steel is subject to pitting and crevice corrosion, so 316 stainless steel, which has molybdenum additions to limit this attack, was developed. Many organizations no longer use 304 stainless and consider 316 stainless to be their basic stainless steel for most process equipment applications.

Unfortunately, both of these alloys can become “sensitized” by improper welding procedures. Sensitization is caused by the formation of chromium carbides in grain boundaries. This reduces the chromium available to form protective passive films and results in localized grain boundary corrosion, primarily in the HAZs near welds. There are two alloying approaches to minimize this problem. One approach is to limit the carbon in the alloy. Types 304L and 316L stainless steel have lower maximum carbon contents, 0.03% C instead of 0.08% C, and this lowers the severity of sensitization. Another approach to the sensitization problem is to add “carbide getters” to the alloy. Types 321 and 347 stainless steel have titanium or niobium (which is also called columbium) added to the alloy. These alloys preferentially form titanium or niobium carbides instead of chromium carbides, and this limits sensitization. Market considerations led North American steel producers to prefer to sell low-carbon stainless steels, while European producers have tended to use titanium or niobium additions. Recent consolidations in the steel industry may change this pattern in the future.

Carbon in austenitic stainless steels serves to strengthen these alloys. The reduction of carbon in the low-carbon grades (304L and 316L) leads to substantial reductions in yield strength. The ASTM specified yield

strength for 304 (UNS S30400) stainless is 30 ksi (207 Mpa) compared to 25 ksi (173 Mpa) for 304L (UNS S30403).<sup>60</sup> Most suppliers now deliver dual-certified alloys, for example, S30403/S30400 or S31603/S31600. These products are clean enough to meet the low-carbon standards of one specification and are strong enough to meet the higher-strength requirements of the other. The tensile strengths discussed above are minimum strengths for fully annealed alloys, and most austenitic stainless steels have much higher yield strengths depending on forming method and application.

Alloy UNS S31700 (317 stainless steel) and the low-carbon version UNS 31703 (317 SS) are less popular than the 316 and 316L stainless grades, but they are becoming more widely used. The alloy contents shown in Table 4.7 are simplifications of the actual standards and, with the exception of the carbon content maximums, are averages between the specified maximum and minimum contents. As steel making controls have improved, the delivered alloys are likely to be very close to the minimum specified content for expensive additions like chromium and nickel. Alloys 317 and 317L have higher specified chromium, nickel, and molybdenum contents and are therefore more corrosion resistant in most environments.

The alloys shown in Table 4.7 are only a representative sampling of the austenitic stainless steels that are available. Other austenitic alloys are available that are more suitable for machining, high-temperature pressure vessels, or welding. Most of them also have standardized UNS numbers.

**TABLE 4.8 Nominal Composition of Selected Highly Alloyed Austenitic Stainless Steels**

USN	Name	C max	Cr	Ni	Mo	Cu	Minimum PREN <sup>a</sup>
S31254	254SMO	0.02	20	18	6.25	0.75	29.5
N08029	20 Cb3	0.07	20	35	2.5	3.5	29
N08367	AL6XN	0.03	21	24.5	6.5		20
N08904	904L	0.02	21	25.5	4.5	1.5	32

<sup>a</sup> The compositions shown in this table are the averages between the minimum and maximum levels. PREN numbers are calculated based on minimum numbers.

Austenitic stainless steels are widely used in heat exchangers, pressure vessels, and process equipment. NACE MR0175/ISO15156 prescribes environmental limits for austenitic stainless steels for use in seal rings and gaskets, compressors, gas lift service, and for special components such as valve stems, pins and shafts, surface and downhole screens, control-line tubing hardware (e.g., set screws), injection tubing, and injection equipment.

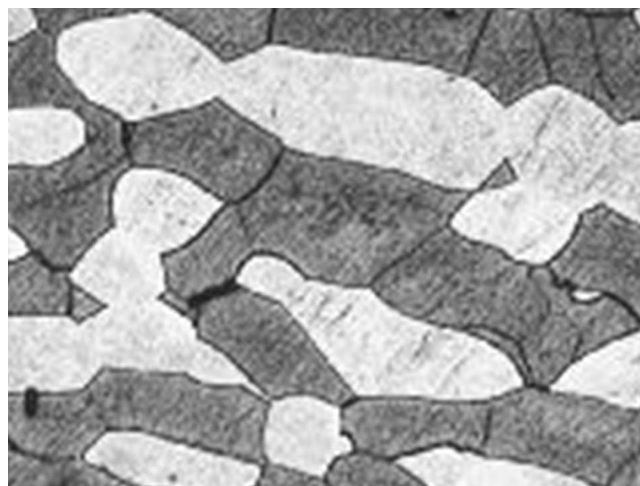
Austenitic stainless steels are considered to be nonmagnetic alloys, but they can have some magnetism due to delta ferrites, which are often present in welds.

**Highly Alloyed Austenitic Stainless Steels** These alloys are frequently called superaustenitic stainless steels, and some of them have such high alloying content that they no longer fit the strict definition of steel, which refers to iron-based (more than 50% iron) alloys. Table 4.8 shows some of these alloys.

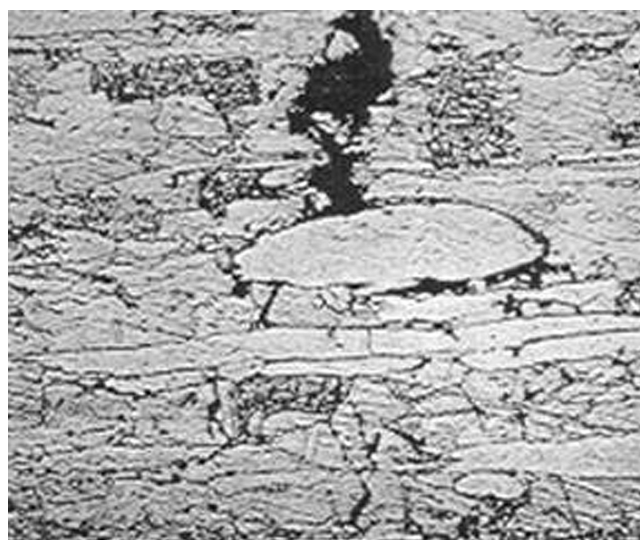
Like all austenitic alloys, these metals can only be strengthened by alloying and, in thin sections, by cold working.

These alloys are used in similar applications to those for austenitic or duplex stainless steels where the environment is considered to be more aggressive.

**Duplex Stainless Steels** The duplex stainless steels have a mixture of BCC ferrite crystals and FCC austenite crystals. The relative percentage of each phase depends on the alloy chemistry, but most of these alloys are intended to have approximately equal amounts of each phase in the alloy. Duplex stainless steels may have similar pitting corrosion resistance to austenitic stainless steels, but their stress corrosion cracking resistance is often superior. Austenite is susceptible to chlorides, and ferrites may crack in H<sub>2</sub>S environments. This is shown in Figure 4.29. The combination of both phases in one alloy means that cracks that initiate in one phase are often blunted and stopped once they reach the other phase (Figure 4.30). Nonetheless, their use is sometimes limited to a maximum temperature of 65°C (150°F) in the presence of chlorides.



**Figure 4.29** Microstructure of a duplex stainless steel. The dark phase is ferrite and the light phase is austenite.



**Figure 4.30** Stress corrosion cracking in duplex stainless steel.<sup>61</sup>

**TABLE 4.9 Nominal Composition of Selected Duplex Stainless Steels**

UNS Number	Common Name	Type	C max	Cr	Ni	Mo	Fe	N	Minimum PREN <sup>a</sup>
S31803	2205	Duplex stainless steel	0.03	23	5.2	3	Bal	0.15	31
S32750	2507	Super duplex stainless steel	0.03	25	7	4	Bal	0.28	38

<sup>a</sup> The compositions shown in the table are the averages between the minimum and maximum levels. PREN numbers are based on minimum numbers.

**TABLE 4.10 Nominal Composition of Selected Precipitation-Hardening Stainless Steels**

UNS	Name	C max	Fe	Cr	Ni	Mo	Other	Comments
S66286	A286	0.08	bal	14.75	25.5	1.25	Ti = 2.12, B 0.001 to 0.01, V 0.10 to 0.50	Austenitic
S17400	17-4 PH	0.07	bal	16.25	4.0			Martensitic
S15500	15-5 PH	0.07	bal	14.75	4.5		Cu = 3.5	Martensitic
S15700	PH 15-7 Mo	0.09	bal	15	7	2.5		Martensitic

Table 4.9 shows the two most commonly used duplex stainless steels. NACE RP0175/ISO15156 requires that duplex stainless steels used in H<sub>2</sub>S service be solution annealed (brought to thermodynamic equilibrium) condition.<sup>12</sup> This limits their strength but improves their corrosion resistance.

Duplex stainless steels are used for a wide variety of subsurface applications. Alternatives to the use of duplex stainless steels include superaustenitic stainless steels and, for lower cost and less corrosion resistance in many environments, austenitic stainless steels such as 317L.

Welding is important with duplex stainless steels to avoid the unwanted formation of brittle sigma phase, which also causes depletion of chromium from the surrounding austenite and can cause sensitization to intergranular corrosion. They can also form a chromium-rich  $\alpha'$  (alpha prime) phase at temperatures from 300°C to 600°C (572°F to 1112°F) known as 475°C embrittlement.<sup>62</sup>

**Precipitation-Hardened Stainless Steels** Precipitation-hardened stainless are chrome-nickel alloys having less nickel than austenitic stainless steels. They can be either austenitic or martensitic in their annealed condition. In most cases, the hardening process to produce high-strength involves heat treatment to produce a high-martensite alloy. If they are to be used in H<sub>2</sub>S service, they must then be tempered to remove the brittle martensite and convert it into tempered martensite, a fine-grained ferrite-plus-austenite structure.

Table 4.10 shows common grades of precipitation-hardening stainless steels. A chief advantage of precipitation-hardening stainless steels is that they can be machined to close dimensional tolerances and then

heat-treated for mechanical strength with minimal distortion. These alloys are normally available in forgings and similar products and are used for wellhead equipment, control devices, and similar applications. Their reduced alloying content when compared with many other CRAs limits their use in thin sections, and they are not normally supplied in tubular form. NACE0175/ISO15156 lists a number of typical applications and the temperature and environmental limits placed on these alloys in low partial-pressure H<sub>2</sub>S service. The same standard also prescribes different maximum hardness levels depending on alloy and application.<sup>12</sup>

Precipitation-hardening stainless steels are considered to be intermediate in corrosion resistance between martensitic stainless steels and the austenitic and duplex stainless alloys. The most common of these alloys in oilfield use is UNS S17400 (17-4 PH).

### Nickel-Based Alloys

There are two different types of nickel-based alloys, solid-solution alloys and precipitation-hardened alloys. Pure nickel and the solid-solution alloys are FCC in structure and, similar to austenitic stainless steels, they are ductile but limited in the strength they can obtain. This is less of a limitation for upstream oilfield operations, which tend to be confined to temperatures of 450°F (230°C) and less, than in processing and refining where high-temperature processing is common and high-temperature strength is important.

Table 4.11 shows selected nickel-based alloys. These alloys tend to be more expensive than the iron-based alloys discussed above, and their use tends to be restricted to very corrosive environments where other alloys are unsuitable.

**TABLE 4.11 Nominal Composition of Selected Nickel-Based Alloys**

USN	Name	Cr	Ni	Mo	Cu	Fe	Other	Comments
Selected solid solution alloys available as tubular products								
N04400	400		66		bal			
N06022	C-22	21	bal	13.5		4	W = 3	
N06255	SM2550	24.5	49.5	7	—	bal	—	
N06625	625	21.5	bal	9			Nb = 3.65	
N06985	G3	22.3	bal	7	2.0	19.5	—	
N08028	28	27	31	3.5	1			
N08032	NIC 32	21.5	32	4.5	—	bal	—	
N08042	NIC 42M	21.5	42	6	2.2	bal	Ti = 0.9	
N08825	825	21.5	42	3	2.2	bal	Ti = 0.9	
N10276	C276	15.5	bal	16	—	5.5	W = 3.8	
Selected precipitation-hardening alloys								
N05500	K-500		66		bal		Ti = 0.6, Al = 2.7	High-strength version of N04400 used for bolts and other high-strength applications
N07718	718	19	52.5	3		bal	Nb = 5.1, Ti = 0.9, Al = 0.5	API SPEC6A718 has additional requirements to avoid embrittling phases
N07725	725	20.7	57	8.3		bal	Nb = 3.4, Ti = 1.4	
N07750	X-750	15.5	bal	—	1	7	Nb = 3.3, Ti = 2.5, Al = 0.7	
N09925	925	21.5	42	3	2.3	bal	Ti = 2.2, Al = 0.3	

**TABLE 4.12 Nominal Composition of Selected Cobalt-Based Alloys**

UNS Name	Name	Cr	Ni	Co	Mo	Fe	Mn	W
R30003	Elgiloy	20	15.5	40	7	bal	2	
R30004	Havar	20	13	42.5	2.4	bal	1.6	2.8
R30035	MP-35N	20	35	bal	9.7			

**Solid-Solution Nickel-Based Alloys** These alloys tend to be used for process equipment and similar topside applications where their relatively low strength, due to their single-phased FCC structure, is less important. They are also used for downhole tubular goods.

**Precipitation-Hardening Nickel-Based Alloys** Precipitation-hardening nickel-based alloys can be fabricated into high-strength components such as bolts and other fasteners.

Unfortunately, these high-strength grades can be subject to hydrogen embrittlement, even the relatively low levels of hydrogen produced on bare metal surfaces due to seawater cathodic protection systems.<sup>63–65</sup> Common applications for these higher-strength nickel-based alloys include wellhead and Christmas tree components, excluding bodies and bonnets, valve and choke components, springs, and bolts.

Both groups of nickel-based alloys find extensive use in seawater applications where their resistance to

crevice corrosion and pitting allows their selection for seawater piping, pump shafts and impellers, valves, and valve inserts.

### Cobalt-Based Alloys

The relatively expensive alloys listed in Table 4.12 are used in very corrosive environments and situations where little or no corrosion can be tolerated. They can be used in H<sub>2</sub>S service in the cold-worked and age-hardened condition at hardnesses up to HRC 55–60 for use in diaphragms, pressure-measuring devices, seals, and springs.<sup>12</sup>

Cobalt-based alloys are finding increased use in wire-line and downhole instrumentation packages. The wire-line must be allowed to degas at surface temperatures for several days to allow dissolved hydrogen to be released. Carbon steels and other very-high-strength alloys might not be suitable in these environments,

**TABLE 4.13 Nominal Composition and Mechanical Properties of Selected Titanium Alloys**

UNS Number	ASTM Grade	Alloy Composition	Minimum Tensile Strength		Minimum Yield Strength		Sour Service Approved? <sup>a</sup>
			ksi	MPa	ksi	MPa	
Alloys Primarily Chosen for Corrosion Resistance							
R50250	1	Unalloyed Ti	35	240	25	170	Yes
R50400	2	Unalloyed Ti	50	345	40	275	
R50550	3	Unalloyed Ti	65	450	55	380	
R50700	4	Unalloyed Ti	80	550	70	480	
R52400	7	Ti-0.15Pd	50	345	40	275	Yes
R52250	11	Ti-0.15Pd	35	240	25	170	
R52402	16	Ti-0.05Pd	50	345	40	275	
R52252	17	Ti-0.05Pd	35	240	25	170	
R53400	12	Ti-0.3-Mo-0.8Ni	70	480	50	345	
Alloys Primarily Chosen for Mechanical Properties							
R56400	5	Ti-6Al-4V	130	895	120	825	Yes
R56401	23	Ti-6Al-4V ELI	115	790	110	755	
R56405	24	Ti-6Al-4V-0.05Pd	130	895	120	825	
R56403	25	Ti-6Al-4V-0.5Ni-0.05Pd	130	895	120	825	
R56323	28	Ti-3Al-2.5V-0.1Ru	90	620	70	480	
R56404	29	Ti-6Al-4V-0.1Ru	120	825	110	755	
R56260	<sup>b</sup>	Ti-6Al-6Mo-2Sn-4Zr	170	1170	160	1100	
R58640	<sup>b</sup>	Ti-3Al-8V-6Cr-4Mo-4Zr	170	1170	160	1100	

<sup>a</sup> Listing as sour service approved means that the alloy is listed in Table D.11 of NACE/ISO15156, Part 3 for Corrosion-Resistant Alloys.

<sup>b</sup> No assigned ASTM titanium grade.

even for the limited times associated with these applications.

### Titanium Alloys

Titanium applications in the oil field are of two types. Most titanium is used because of the alloys' excellent resistance to corrosive environments. These applications tend to be topside and primarily in water-handling systems where their corrosion resistance is an advantage in seawater piping and heat exchangers. Sometimes, titanium is used for downhole or subsea applications where the corrosion resistance, while still excellent, is less important and the strength-to-weight ratio of titanium, the highest of any commercially available alloys, becomes the reason for their choice. Table 4.13 shows typical titanium alloys used for both corrosion resistance and for mechanical properties reasons.

Corrosion-resistance applications tend to use commercially pure titanium (Ti grades 1–4) or, for heat exchangers and other complicated devices, titanium alloyed with palladium, which greatly improves the crevice corrosion resistance at elevated temperatures. Ruthenium is also added to titanium alloys for the same

purposes and is considered to be a less expensive crevice corrosion addition.

The thermal conductivity of titanium is lower than for other commonly used heat exchanger tubing alloys. This means that titanium is frequently used with thinner gages than other alloys. The excellent corrosion resistance allows for this reduction, but heat exchanger tubing bundles frequently fail by fatigue caused by the turbulent fluid flow past their surfaces. The flexibility of titanium tubes must be accommodated by supplying more support baffles than would be required for some other tubing alloys.

Titanium plate-frame heat exchangers are often used offshore because they offer significant weight savings over other materials.<sup>66</sup> The relatively high strength of titanium allows operation at pressures that cannot be achieved with aluminum heat exchangers, which offer similar weight savings.

While titanium alloys have generally good corrosion resistance, there are several cautions that should be observed with their use. Titanium will be cathodic to most other alloys. Depending on the relative size of the other metal, galvanic corrosion of the other alloy, typically carbon steel, will result. Unfortunately, hydrogen



**TABLE 4.14 Selected Uses of Titanium in Offshore Oil and Gas Production<sup>67</sup>**

Application	Company	Project	Titanium Alloy Grade
Taper stress joints	Placid Oil	Green Canyon	23 (Ti-6Al-4VELI)
Taper stress joints	Ensearch	Garden Banks	23
Taper stress joints	Oryx Energy	Neptune	23
Fire water systems	Norsk Hydro	Troll B (Oil)	2 (commercially pure)
		Brage, Visund	
Fire water systems	Elf Petroleum	Froy TCP	2
Fire water systems	Statoil	Sleipnir West, Siri	2
Fire water systems	Statoil	Norne	2
Seawater lift pipes	Statoil	Sleipnir	2
		Veslefrikk	2
Ballast water systems	Mobil	Statfjord A/B	2
		Beryl	
Ballast water systems		Hibernia	2
Penetration sleeves	Statoil	Sleipnir West	2
Penetration sleeves	Norsk Hydro	Oseberg	2
Penetration sleeves	Mobil	Statfjord	2
Freshwater pipework	Elf	Frigg	2
Seawater pipework	Esso	Jotun	2
Seawater pipework	Norsk Hydro	Njord, Visund	2 (110 tons)
Seawater systems, fire, ballast, and produced water pipework	Statoil	Asgard B	2 (300 tons)
Gravity-based system	Statoil	Troll A (Gas)	2(500 tons)
Drilling riser	Statoil (Conoco)	Heidrun	23
Booster lines	Statoil (Conoco)	Heidrun	9 (Ti-3Al-2.5V)
Anchor system pipework	Statoil (Conoco)	Heidrun	2
Penetrations and manholes	Statoil (Conoco)	Heidrun	2

embrittlement of the cathodic titanium can also occur. Most organizations have decided to not mix metal systems, and it is common for seawater piping systems, heat exchangers, and ancillary equipment to be constructed from titanium to avoid any galvanic coupling problems.

Other environments that cause corrosion problems include hydrofluoric and uninhibited hydrochloric acidizing treatments. Methanol can cause stress corrosion cracking, although the presence of water will inhibit this corrosion.

Table 4.14 shows representative uses of titanium in offshore applications.

Titanium alloys are difficult to weld and require special cleaning procedures to insure that an oxide-free surface is available during welding and that the weld bead does not oxidize and prevent adequate fusion to the parent metal.

### Copper Alloys

Pure copper is FCC and very ductile but has low yield and tensile strengths. For these reasons, pure copper is

only used for electrical conductivity and for electrical conduit. Piping and other structural applications are made from one of several alloy groups. Copper alloys have better thermal conductivity than other alloys, and this makes them the alloy system of choice for many heat-transfer applications, although their relative weight and erosion-corrosion susceptibility sometimes justifies the use of titanium, aluminum, or stainless steel for these applications. Copper alloys also have natural biofouling resistance, and this means that copper alloys are often used for piping systems where fouling cannot be tolerated, for example, stagnant seawater firewater piping.

Copper-based alloys have three major environmental limitations, and extensive research has been devoted to alloy development and design methods to minimize these limitations. Dealloying, the loss of one constituent of an alloy leaving an altered residual structure, is a potential problem for most copper-based alloys. This has been minimized by alloying addition controls and by the development of more resistant alloy systems, for example, cupronickels, which, while not immune to this problem, are much less likely to have the problem than the earlier copper-zinc brasses which they have largely

**TABLE 4.15 Nominal Compositions of Selected Copper Alloys**

UNS Number	Name	Cu	Al	Sn	Zn	Ni	Other
<i>Wrought Copper Alloys</i>							
C17200	Copper-beryllium	bal					Be = 2, Cu + Ni $\geq$ 0.2, Co + Ni + Fe $\leq$ 0.6
C44300	Admiralty brass	71		1	28		
C46400	Naval brass	60		0.8	39.2		
C2600	Cartridge brass	70			30		
C26130	Arsenical 70/30 brass	70			30		As = 0.05
C28000	Muntz metal, 60%	60			40		
C61300	Aluminum bronze	92.65	7	0.35			
C61400	Aluminum bronze	91	7				Fe = 2
C63000	Nickel aluminum bronze	82	10			5	Fe = 3
C68800	Aluminum brass	73.5	3.4		22.7		Co = 0.4
C70600	Cupronickel, 90-10	90				10	
C71500	Cupronickel, 70-30	69.5				30	Fe = 0.5
C72200	Cupronickel plus Cr	82.2				16.5	Cr = 0.5, Fe = 0.8
<i>Cast Copper Alloys</i>							
C86300	Manganese bronze	63	6		25		Fe = 3, Mn = 3
C90300	Tin bronze	88		8	4		
C90500	Tin bronze	88		10	2		
C90700	Tin bronze	89		11			
C95400	Aluminum bronze	85	11				Fe = 4
C95500	Nickel aluminum bronze	80	11			4.3	Fe = 4
C95800	Nickel aluminum bronze	81	9			5	Fe = 4, Mn = 1
C95900	Aluminum bronze	bal	12.8				Fe = 4
C96200	Cast copper-nickel	88.6				10	Fe = 1.4

replaced for many condenser, heat exchanger, and piping applications.<sup>68,69</sup> Copper alloys are also subject to stress corrosion cracking in ammonia-containing environments. The third limitation is erosion corrosion. Maximum allowable fluid velocities are much lower for copper alloys than for carbon steel and most other, usually stronger and harder, alloys.

NACE RP0175/ISO 15156 places no restrictions on the use of copper-based alloys in H<sub>2</sub>S environments. This document, which addresses cracking problems associated with H<sub>2</sub>S, does comment that, while many copper-based alloys have been used successfully in downhole environments, they can suffer other forms of corrosion in sour oilfield environments, particularly if oxygen is present.<sup>12</sup> The reference to oxygen is very important. Unlike most other oilfield alloys, copper is resistant to acids, because the equilibrium potential for copper is noble to the hydrogen reduction reaction at all pHs, and oxygen is the most likely source of a reducible chemical to balance corrosion-related oxidation of the metal. Unfortunately, copper-based alloys have alloying additions that depend on passive films to limit corrosion, and these alloys can corrode in some acids, although the corrosion rate is often very slow.

Some representative copper-based alloys are listed in Table 4.15.

**Wrought Copper-Based Alloys** Most wrought copper-based alloys are used for piping systems and heat transfer, for example, water-cooled condensers. At one time, most wrought copper-based alloys were brasses made from alloying copper with zinc. Zinc strengthened the alloy, but it lowered the overall corrosion resistance and made the alloy subject to dezincification, a form of dealloying. In recent years, the trend has been to use copper-nickel alloys for most condensers and other copper-based piping systems, especially in seawater service.<sup>70</sup>

All copper alloys are considered to have excellent antifouling characteristics, and this makes them desirable for firewater systems, where fouling in stagnant seawater could lead to debris plugging nozzles and other tight restrictions during emergencies. Unfortunately, most metals, to include copper alloys, are subject to underdeposit attack, a form of crevice corrosion. This is shown in Figure 4.31 for 90-10 cupronickel (UNS C70600) tubing removed from an offshore platform firewater system. The tubing corroded at the 6 o'clock position due to debris collecting at this location. Problems like this have led some organizations to specify fiberglass and similar materials for firewater systems in recent years. The smoothness of the plastic piping interior retards biofouling attach-



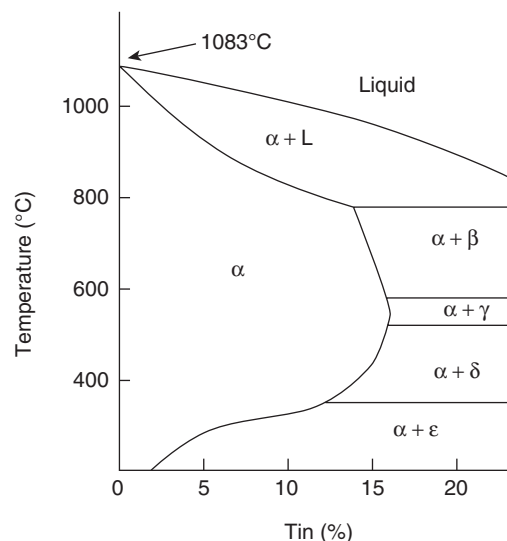
**Figure 4.31** Under deposit corrosion of 90-10 cupronickel tubing in offshore Gulf of Mexico firewater system.

ment and polymers are not susceptible to underdeposit attack.

Aluminum brass, which is a copper-zinc alloy with aluminum additions, was at one time used onshore in freshwater for erosion-corrosion resistance near condenser tube inlets, but this is no longer the practice for large condensers.<sup>70</sup> Velocity limits to prevent erosion in copper-based piping systems vary from 4 ft/sec (1.2 m/s) for pure copper up to 15 ft/s (4.5 m/s) for 70-30 cupronickel (UNS C71500).<sup>71</sup>

Copper-beryllium alloys (e.g., UNS C17200) are unusual for copper-based alloys, because they are very strong. Yield strengths for UNS C17200 can range from 32–100 ksi (220–700 MPa) depending on component size and heat treatment. Oilfield applications are primarily for nonsparking tools. The tools are not as strong as steel tools and wear out faster, but their increased cost is justified for safety reasons. Copper-beryllium alloys are also used for nonmagnetic measurement-while-drilling tools for directional drilling, both downhole and in pipelines. A partial list of other oilfield applications includes nonmagnetic drill string components, subsea valve gates, springs, and fasteners.

**Cast Copper-Based Alloys** At one time, most cast copper-based alloys were copper-tin alloys called bronzes. Today, the term bronze is applied to a wide variety of copper-based alloys having little or no tin. Bronze most often refers to copper-based alloy systems where the major alloying element is neither zinc (brasses) nor nickel (cupronickels). The relative scarcity of tin and the associated high costs of copper-tin alloys have led to the development of aluminum bronzes (copper-based alloys with aluminum additions) and nickel-aluminum bronzes.



**Figure 4.32** The copper-tin phase diagram.

While bronzes are available as wrought products, they are most commonly used for castings. The phase diagrams all bronzes are similar to the copper-tin diagram shown in Figure 4.32. The melting temperatures of bronzes drop much quicker for these alloys than for brasses and cupronickels. This makes them easier to melt and pour. Equally important, the low-temperature microstructure of these alloys is two-phased, which means that, compared with brasses and cupronickels, they are harder and are more erosion-resistant. Thus, they are better suited for the complicated geometries and fluid flow patterns found in pumps, valves, and similar equipment. The relative thickness of castings compared to fluid transfer piping and heat-transfer tubing means that any reduced corrosion resistance of these alloys can usually be tolerated.

The most common alloys for large seawater pumps are nickel-aluminum bronzes (e.g., UNS C95500 or C95800). Foundry practice for these alloys is critical, because they can form unwanted microstructures that are subject to selective phase attack, a form of dealloying.<sup>72–74</sup>

Copper alloys are acceptable in accordance with the NACE Standard MR01575/ISO15156 guidelines for environmental cracking in oilfield  $H_2S$  service. The latest version of the standard says that copper alloys have been used without restrictions on the key environmental parameters of  $H_2S$  concentration, chloride concentration, and pH. However, the same standard cautions that environmental degradation, such as weight loss corrosion, may be a problem, particularly if oxygen is present. Furthermore, the standard cautions that some copper-based alloys may be susceptible to galvanically induced hydrogen stress cracking (GHSC).

The lack of published literature on copper alloys in aggressive wellbore environments led to a laboratory study of several copper alloys under consideration for gate valve and wellhead applications. The overall corrosion rates for the copper-based alloys tested, aluminum bronze (UNS C63000 and C62730), beryllium-copper alloy (UNS C17200), and copper-nickel alloy (UNS C96900) were substantially higher (by orders of magnitude) than for the baseline alloys, 17-4PH stainless steel (UNS S17400), type 410 stainless steel (UNS S41000), type 660 stainless steel (UNS S66286), nickel-based alloy 718 (UNS N07718), and nickel-based alloy 625 (UNS N06625), tested in the same production-simulation environments.<sup>75</sup> This laboratory exposure test at 350°F (177°C) suggests that copper-based alloys should not be used in aggressive high-temperature H<sub>2</sub>S environments. The use of the same alloys at lower temperatures and pressures may be acceptable, but testing in accordance with a testing protocol such as recommended by NACE or other standards is advisable.

### Aluminum Alloys

Aluminum alloys have had limited uses in upstream oilfield operations, but their use is increasing. Aluminum is a very reactive metal, and the natural oxide film that forms on aluminum surfaces is usually much thicker than on the other CRAs discussed in this chapter. This makes aluminum very resistant to atmospheric corrosion, even in marine environments.

Aluminum has several other very desirable characteristics. Many aluminum alloys have high strength-to-weight ratios. This is a major advantage for offshore platform topside structures such as helicopter decks (helidecks) and modular crew quarters and offices. It is ductile at low, even cryogenic temperatures. This makes aluminum piping and process equipment an excellent choice for LNG processing and similar low-temperature applications.

Unfortunately, aluminum is also an amphoteric metal, which means it corrodes much faster in both acidic (low pH) and caustic (high pH) environments. High-pH environments are relatively less important, because most minerals have limited solubility at high pHs and the metal tends to stay dry underneath a protective mineral scale, but many production fluids have low pHs, making aluminum unsuitable for some applications. Aluminum alloys have no restrictions on cracking susceptibility in H<sub>2</sub>S environments.<sup>12</sup> This is somewhat surprising, because aluminum is known to suffer hydrogen embrittlement in some environments.<sup>76,77</sup> Aluminum is also subject to liquid metal embrittlement, and mercury must be removed from



**Figure 4.33** Aluminum corrosion at the six o'clock position where acidic atmospheric condensate water collected in a low-temperature ventilation system.

natural gas streams before they enter aluminum piping and heat exchangers.<sup>78</sup>

Aluminum is often used for jacketing thermally insulated piping. Moisture ingress can cause corrosion at the 6 o'clock position where liquid collects and is exposed to moist air containing CO<sub>2</sub>. (Therefore, components should be designed to allow moisture to escape, usually through drainage holes placed at regular intervals along the bottom of the jacketing.) A similar situation is shown in Figure 4.33, which shows corrosion at the bottom of an aluminum moist air ventilation tube.

**Aluminum Alloy Designations** The alloy designation system for aluminum alloys requires a chemistry designation and a temper designation. Most industrial users use the system developed by the Aluminum Association in North America. An abbreviated version of these classifications is shown in Table 4.16. The table only shows the alloy designations for wrought alloys, but the system for cast alloys is very similar. In both cases, a complete specification would describe the chemistry and temper in a single number, for example, aluminum 6061-T6, which is the most-commonly specified heat-treatable alloy of aluminum in the usually specified strongest temper.

The most-commonly used wrought aluminum alloys are listed in Table 4.17. Note that each alloy has both a chemistry designation and one or more typical temper designations. The UNS numbers for these alloys are also listed, although they are seldom used except in the writing of international standards. The UNS system does not allow for temper designations, although some users will simply add the temper designation to the

**TABLE 4.16 Wrought Aluminum Alloy Designation Systems**

Numbering System for Wrought Aluminum Alloys Used in Oil and Gas Production		
1xxx	Super- or commercial-purity aluminum	Not heat treatable, used as corrosion-resistant cladding on stronger aluminum alloys
2xxx	Copper is the major alloying addition	Heat treatable
3xxx	Manganese is the major alloying addition	Work hardening
4xxx	Silicon is the major alloying addition	Work hardening, but Al-Si alloys are usually used as castings (4xxx alloys are typically the cladding for braze clad products)
5xxx	Magnesium in the major alloying addition	Work hardening
6xxx	Magnesium and silicon are the major alloying additions, usually at approximately 2:1 magnesium to silicon	Heat treatable
Temper Designations for Wrought Aluminum Alloys		
F	As fabricated, with no specified control over hardening processes	
O	Annealed to soft state	
H	Strain hardened	
H1	Strain hardened only	
H3	Strain hardened and stabilized	
H32/H34	Strain hardened and stabilized to ¼ hard (H32) or ½ hard (H34) condition	
H116	For 5xxx alloys in marine service, this temper is for alloys that have been strain hardened as the final operation in manufacture and meet specified levels of exfoliation and intergranular corrosion.	
H321	For 5xxx alloys in marine service, this temper is for alloys that have been thermally stabilized as the final operation in manufacture and meet specified levels of exfoliation and intergranular corrosion.	
T	Thermally treated for mechanical properties	
T5	Cooled from hot working and thermally aged	
T6	Solution treated and thermally aged	

**TABLE 4.17 Typical Wrought Aluminum Alloys Used in Oil and Gas Production**

UNS Number	Aluminum Association Number	Typical Use
A92024	2024-T6	Drill pipe
A92014	2014-T6	Drill pipe
A93105	3105-H14	Thermal jacketing for insulated piping
A93003	3003-H14	Housing/office modules, thermal jacketing for insulated piping, and brazed aluminum heat exchanger components
A95052	5052-H32 or -H34	Housing/office modules and brazed aluminum heat exchanger components
A95083	5083-H116 or -H321	Plate for helidecks, hulls for workboats, and brazed aluminum heat exchanger components
A95086	5086-H116 or -H321	Plate for helidecks, hulls for workboats, and brazed aluminum heat exchanger components
A95454	5454-H32 or -H34	Plate for helidecks, hulls for workboats, and brazed aluminum heat exchanger components
A95456	5456-H116 or -H321	Plate for helidecks, hulls for workboats
A96061	6061-T5 or -T6	Extrusions for railings and ladders, and brazed aluminum heat exchanger components
A96063	6063-T5 or -T6	Extrusions for railings and ladders, and brazed aluminum heat exchanger components
A96005	6005-T5 or -T6	Extrusions for railings and ladders
A96105	6105-T5 or -T6	Extrusions for railings and ladders
A96082	6082-T5 or -T6	Extrusions for railings and ladders



alloys, for example, Aluminum Association alloy 5052-H32 would be UNS A95052H32.

Note that the aluminum alloys fall into two groupings—those that can be thermally treated for strength and those that can only be strain-hardened (work-hardened). Sheet and plate aluminum alloy components are typically the work-hardened 3xxx and 5xxx alloys, while extrusions for structural members and tubular products are typically produced from the thermally treated (age-hardened) 6xxx alloys.

**Typical Applications for Various Aluminum Alloy Groups** Commercially pure aluminum alloys, the 1xxx group, are the most corrosion-resistant alloys. They are so soft that they are not used in oilfield applications except as corrosion-resistant surfaces on clad structural-alloy plate.

Most users consider the 5xxx and 6xxx alloys to be the most suitable for marine applications, and their use in nonmarine applications is also widespread. A typical workboat or helideck would have plate components of 5xxx alloys and the supporting structure/frame made from 6xxx alloys. Aluminum fasteners could also be made from 6xxx alloys, but aluminum has serious galling problems, and it is common to use specially designed connections when mechanically joining aluminum structural components.

Clad aluminum alloys are available. They were originally developed with commercially pure aluminum surfaces for corrosion control over stronger structural aluminum alloy plate. Many complex aluminum heat exchangers, to include those used in oilfield heat exchangers, have low-melting temperature exteriors with structural alloys in the center. These clad products are used to manufacture brazed aluminum structures such as heat exchangers.

Brazed aluminum heat exchangers are frequently used offshore for gas processing. The parting sheets, which separate the fluids, are usually made from 3xxx alloys, and they are brazed together using a low-melting point aluminum-silicon alloy from the 4xxx series.<sup>79</sup> The aluminum-silicon alloys have very low-melting temperatures in comparison with other aluminum alloys, and they are usually used as castings. They are seldom used for structural purposes in oilfield applications, and this is the reason why they are not listed in Tables 4.16 and 4.17.

Welding of aluminum is possible, but it is more difficult than for carbon steel and other iron-based alloys. Complex machinery and process vessels are factory-welded, but it is common to use mechanical connections in oilfield construction and assembly, for example, of helidecks, while similar structures from carbon steel would be welded.

There have been limited attempts to develop and market aluminum drill pipe. Drill pipe is usually made from 2xxx alloys containing copper as the main alloying addition. The 2xxx alloys have some of the highest fatigue strengths of any aluminum alloys, and this property, combined with their low weight, makes them acceptable for many applications in other industries. They were the first high-strength aluminum alloys developed. Their corrosion resistance, while adequate for many aerospace applications, is not sufficient for oilfield operations, except in circumstances like drill pipe, where they are only exposed to downhole fluids for limited periods of time and can be inspected for corrosion and other damage, typically wear and fatigue cracking, between uses.<sup>80,81</sup>

### Additional Considerations with CRAs

CRAs are used whenever the increased capital cost is justified by reduced maintenance and inspection costs or when increased reliability is necessary. Many high-volume gas wells are so corrosive that carbon steels are not considered, and the question becomes which CRAs should be used. While some gas fields have high-H<sub>2</sub>S levels, most gas well corrosion is due to CO<sub>2</sub>.

Oil fields are generally not corrosive until the water cut increases and/or the system “sours” due to the increased production of H<sub>2</sub>S. For this reason, it is common to specify that all equipment be constructed from materials considered resistant to H<sub>2</sub>S-related cracking in accordance with the appropriate guidelines in NACE MR0176/ISO 15156.<sup>10–12</sup> These precautions do not prevent other forms of environmental degradation, and corrosion can be the unfortunate result.

The increased alloying content of CRAs means that they cost more than carbon steels. A way of reducing costs is to use CRA cladding or lining on carbon steel components. This long-standing practice for wellhead and process equipment has been extended to downhole equipment and tubular goods. The CRA can be applied by a number of processes. If CRAs are mechanically bonded using either explosive bonding or thermal shrinking, the composite structures are referred to as a lined pipe instead of clad pipe.<sup>82</sup>

**Pitting Resistance Equivalent Number (PREN)** Many organizations use the PREN formula in NACE MR 0176/ISO 15156 as a basis for determining the relative corrosion resistance of oilfield alloys. The PREN formula in this standard is:<sup>12</sup>

$$\text{PREN} = w_{\text{CR}} + 3.3(w_{\text{Mo}} + 0.5 w_{\text{W}}) + 16w_{\text{N}}$$

where:

$w_{Cr}$  = the weight percentage of chromium in the alloy;

$w_{Mo}$  = the weight percentage of molybdenum in the alloy;

$w_W$  = the weight percentage of tungsten in the alloy;

$w_N$  = the weight percentage of nitrogen in the alloy.

Larger values of PREN are considered to indicate greater resistance to pitting corrosion. The contribution of other alloying additions, for example, nickel and copper, is not considered in this formula, and most authorities recommend using PREN as a general guideline.<sup>83</sup> It is important to remember that the PRENs shown in NACE MR0175/ISO15156 were included to aid in classifying alloys into different categories. Many experts are of the opinion that they are unreliable indicators of corrosion resistance except in a very general sense; that is, if two alloys have widely separate PRENs, then it is logical to conclude that the higher PREN will indicate greater corrosion resistance, but for numbers that are close, for example, within 5 PRENs, the performance may be affected by alloying parameters not considered by the PREN formula, for example, the nickel content and the microstructure.

Other PREN formulas have been developed for other applications, for example, seawater, but their use is not widespread in oilfield applications.

It is common to rank alloys by PREN and then to consider their relative resistance to cracking in environments of interest. The logic behind this ranking procedure is that alloys will first develop pits that serve as stress raisers for the initiation of subsequent cracking.<sup>84</sup>

**Temperature Criteria** Pitting and crevice corrosion are temperature-dependent, and a number of tests have been developed to determine the temperature at which these forms of corrosion are likely to occur. Most of these tests involve exposing metal samples with artificial crevices to increasing temperatures until a predetermined amount of crevice or pitting corrosion is observed. The idea is to limit the use of an alloy to temperatures where these forms of corrosion are unlikely. Unfortunately, the published data for critical pitting temperatures (CPTs) and critical crevice corrosion temperatures (CCTs) produce widely conflicting data (up to  $\pm 20^\circ\text{C}$  [ $36^\circ\text{F}$ ]), so the use of published data, even if obtained by following an ASTM or other standard, is questionable. Service environments may produce pitting or crevice corrosion at temperatures significantly lower than those determined in controlled

laboratory tests. The best use of these tests is for their intended purpose of ranking alloys insofar as their pitting or crevice corrosion tendencies.<sup>85–87</sup>

**Alloy Selection** The cheapest and fastest method of selecting alloys for corrosive environments is to rely on published information. The drawback to this approach is that changes in environments, even within the same field, can cause significant changes in corrosion resistance.<sup>59</sup> Several NACE standards provide guidance on alloy selection, and these guidelines are often followed.<sup>10–12,82,88,89</sup> Unfortunately, the most commonly followed guidelines, NACE MR0175/ISO15156 Parts 1–3 only cover resistance to hydrogen-related cracking, and many organizations are surprised when materials chosen in accordance with “NACE guidelines” suffer other forms of environmental degradation, for example, pitting or chloride-related stress corrosion cracking.

For aggressive conditions and/or new fields, it is common to select candidate alloys according to the following pattern:

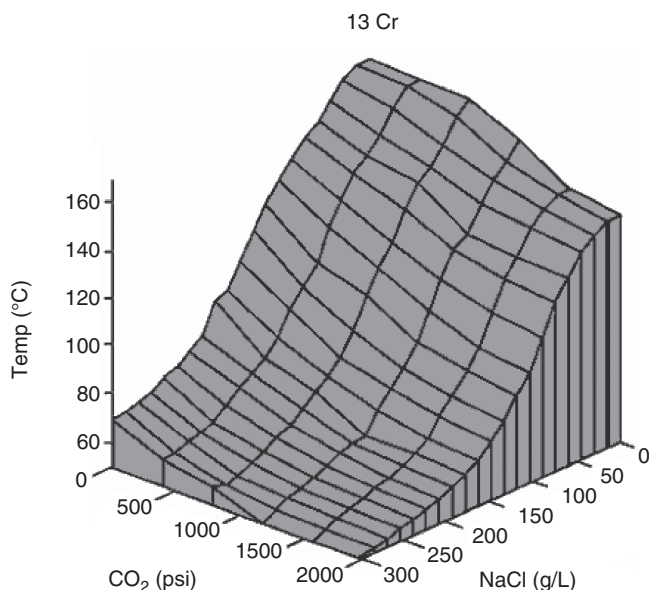
- Selection for general corrosion resistance
- Selection for localized attack resistance
- Selection of CRAs by environmental specification, for example, in accordance with MR0175/ISO15156.<sup>1</sup>

This preliminary selection allows an initial screening of candidate alloys that are then often evaluated in a series of controlled laboratory exposures, in environments as close as possible to the anticipated field conditions, before final alloy selection.<sup>1,59</sup> Important environmental considerations include the aging of a field for oil wells and the presence of organic acids in gas wells.<sup>1</sup>

Note that some alloys, for example, 3xx stainless steels, cannot be used above certain temperatures because of a concern for chloride stress corrosion cracking. These and other alloys cannot be used for downhole tubulars because of strength considerations, and this limits most downhole alloy selections to considerations between carbon steel, stainless steel, and nickel-based alloys.

The most commonly specified CRAs are martensitic stainless steels, commonly referred to as 13Cr or Super-13Cr alloys. They are widely used in downhole applications and for subsea pipelines. They are seldom used for topside surface applications because they are subject to pitting corrosion.

A common progression of alloy selection, useful for high-temperature gas wells and other corrosive environments, is:



**Figure 4.34** Corrosion resistance of 13Cr (UNS S42000) in the absence of oxygen, and H<sub>2</sub>S.<sup>59</sup>

Carbon steels → martensitic stainless steels (13Cr and “Super 13Cr”) → austenitic stainless steels (often limited because of temperature considerations and relatively low strength) → duplex stainless steels → high-nickel austenitic alloys.

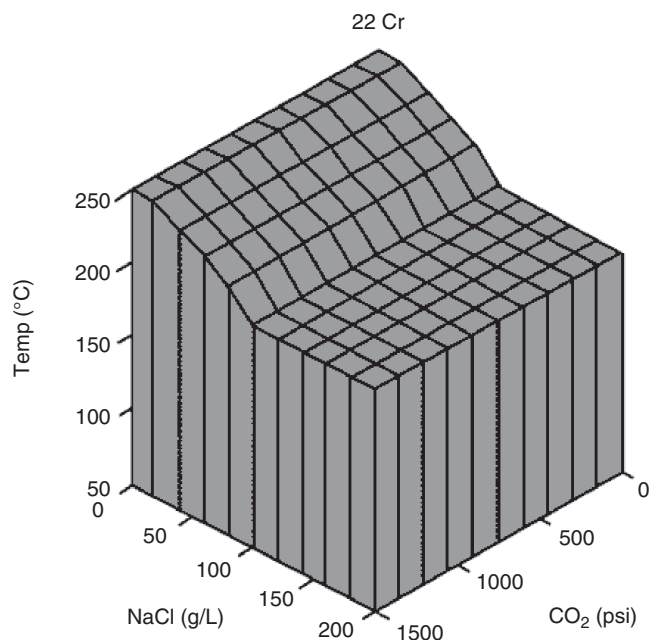
This is reflected in Figures 4.34 through 4.36, which show the results of laboratory tests in simulated oilfield environments. The figures show environments where corrosion rates will be  $\leq 0.05$  mm/year (2 mpy) with no sulfide corrosion cracking or stress corrosion cracking. The limitations shown for these and other nickel-containing alloys are probably conservative.<sup>59</sup>

Other alloy systems are used for specialized applications, both downhole and topside, but these are the most commonly specified alloys for downhole OCTG and other applications.

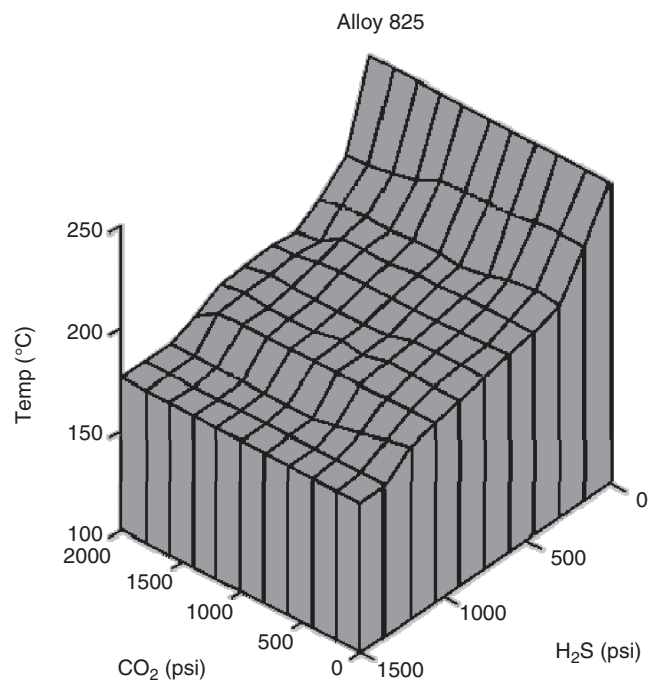
Topside applications have fewer strength-related and temperature-related limitations, and a general summary of the kinds of alloys often used for topside applications is shown in Table 4.18.<sup>88</sup>

## POLYMERS, ELASTOMERS, AND COMPOSITES

Polymers are organic materials consisting of large molecules formed from small precursors called monomers. The term polymer is a combination of the terms poly, signifying many, and mer, which signifies repeat units or molecules of the original monomer(s). Some polymers are homopolymers, polymers made from one monomer type, and others are copolymers, which are



**Figure 4.35** Corrosion resistance of duplex stainless steel 2205 in the absence of oxygen, H<sub>2</sub>S, and elemental sulfur.<sup>59</sup>



**Figure 4.36** Corrosion resistance of nickel based alloy 825 (UNS N08825) in the absence of oxygen, H<sub>2</sub>S.<sup>59</sup>

formed from two or more different monomers which are joined together in large molecules of copolymeric materials. Chemical names for polymers are combinations of the name of the precursor monomer(s) and the prefix “poly,” for example, polyethylene is formed from

**TABLE 4.18 Topside Materials Selection Examples**

Equipment	Typical Material Selection		
Flowlines	Super duplex	UNS S31254 254 SMO	Carbon steel with inhibitors
Produced water	UNS S31254 254 SMO	Carbon steel with inhibitors	Glass reinforced plastic
Flare systems	UNS31603 SS316L	Low temperature—carbon steel	
Water injection	Carbon steel (<5 ppb oxygen)		
Heat exchanger	Titanium	Super duplex	
Chemical injection	Titanium	PVDF-PE	Carbon steel
Firewater	Cupronickel	Glass reinforced plastic	
Gas-cooling heat exchangers	Aluminum		

PVDF-PE, polyvinylidene fluoride–polyethylene.

ethylene monomer. The atomic weight of polymers is typically in the thousands.<sup>3</sup>

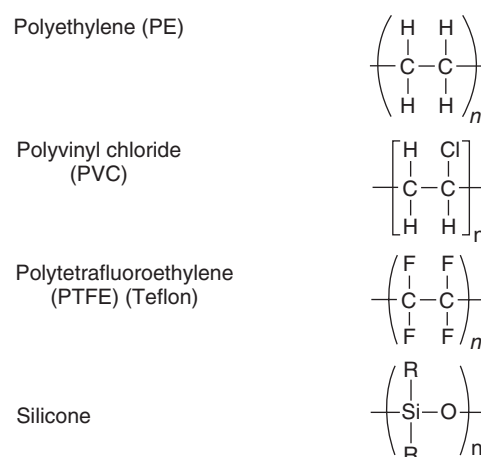
There are a number of ways of classifying polymers. One of the most common is based on their temperature responses. Thermoplastic polymers soften and melt when heated and stiffen and solidify at lower temperatures. By contrast, thermosetting polymers undergo chemical reactions upon heating during manufacture or fabrication and become solids with no melting points. Thermoplastics can be remelted and recycled whereas thermosets cannot be melted once the setting reaction is completed.

Most thermoplastics are long-chain polymers which may become branched but will have limited cross-linking between the chains. By contrast, thermosets have relatively higher amounts of cross-linking, typically 10–50% of the chain repeat units, which leads to stiffening and relatively brittle behavior.<sup>3</sup>

Common oilfield thermoplastic materials include high-density polyethylene (HDPE) and polyvinyl chloride (PVC). Both of these materials are used for oilfield piping, and high-density polyethylene (HDPE) is also used for storage tanks up to several thousand gallons in capacity. Fluoropolymers, commonly referred to by tradenames such as Teflon and Halar are also thermoplastics, even though they can be used at relatively high temperatures. Epoxies are typical thermosetting polymers that are used when hardness is desired. Thermosets also tend to be relatively brittle when compared with thermoplastics.

Elastomers are rubbery, flexible polymers used for o-rings, gaskets, and seals of many types. They usually are made from thermosetting polymers with limited cross-linking. The limited cross-linking allows these materials to deform without breaking and, if the load is released, they recover their original shape.

Plastics are polymers which can be molded or shaped. They are stiffer than elastomers, usually due to higher molecular weights. While all plastics are polymers, many polymers are not plastics, even though the terms are often used interchangeably.



**Figure 4.37** Selected polymer repeat units. The R in the silicone structure stands for a radical. It is usually CH<sub>3</sub>, but other versions of silicone are also available.

The long chains in polymers are normally based on covalent carbon–carbon bonds. The most notable exception is silicones, a class of polymers with silicon–oxygen bonds as the repeat units in the polymer chain. This is shown in Figure 4.37, which shows the structures of several common polymers.

Additives to polymers are used as stabilizers against oxidation and ultraviolet (UV) degradation, flame retardants, fillers, plasticizers in flexible piping, and reinforcements. The presence of these additives means that materials from different suppliers may have different degradation mechanisms and environmental vulnerabilities. This is why NACE and other organizations have developed standards for testing polymers, composites, and elastomers for suitability to various oilfield environments.<sup>89–94</sup>

Unlike metals and ceramics, the mechanical properties of polymers are strongly dependent on loading rates. There are standards for the loading rates to be used in determining hardness and strength, and these differ in some ways from the methods used in



determining similar properties in metals. Virtually all polymers are subject to creep at ambient temperatures, in marked contrast to most metals. This is one reason for the widespread use of reinforcement additives in many polymers.

The increasing use of polymers is primarily due to their relatively good corrosion resistance and, in the case of composites, their excellent strength-to-weight ratios. The smooth surfaces of polymeric piping are also advantageous in minimizing biofouling. This is a major reason why they are increasingly used for firewater systems, where debris from biofouling can plug valves and similar small openings.<sup>95,96</sup>

Polymeric piping is more subject to mechanical damage than metals, and this is the reason why polymeric piping is not used for many above-ground hydrocarbon piping systems. Even composites are more subject to mechanical damage and, unlike metals, composites will tend to fracture instead of bending when overloaded. This has been a major problem with the installation and use of relatively large composite storage tanks. They have been known to crack due to shipping and construction site handling.

All polymers are permeable to gases. This limits their use for storing liquids if air contamination is a concern, for example, produced water intended for reinjection. It also means that polymers will absorb gases and, to a lesser extent, water and small hydrocarbon liquid molecules. Rapid decompression of gaskets, o-rings, and liner materials on metal piping is a concern with their use, and standards for testing and rating these polymers have been developed.<sup>92</sup> Swelling due to absorption of gases and liquids can also occur.

Polymers have relatively low upper temperature limits, and they also become brittle when cold. They should only be used in their prescribed temperature ranges.

Polymer degradation includes UV degradation and chemical attack, which can be swelling, softening due to leaching of additives, or oxidation. The attack can be of the polymer matrix or of additives and reinforcements.

Unfortunately, nondestructive testing methods to monitor polymer degradation are not available beyond routine inspection for swelling or discoloration.

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## FORMS OF CORROSION

### INTRODUCTION

There are many systems for classifying corrosion, but the most common categories follow a pattern popularized by M. Fontana in a series of articles he wrote for *Chemical and Engineering News* in the 1940s and later in the textbook he published while a professor at Ohio State University.<sup>1</sup>

The forms listed in Dr. Fontana's textbook are:

- Uniform attack
- Galvanic or two-metal corrosion
- Pitting
- Crevice corrosion
- Intergranular corrosion
- Selective leaching
- Erosion corrosion
- Stress corrosion
- Hydrogen damage

An advantage of this form of corrosion classification is that it can usually be confirmed by visual inspection, which allows identification of possible remedial measures without laboratory analysis.<sup>1</sup> The reason that the terminology for forms of corrosion described in the above list has gained widespread use is that they are tied to appropriate methods of corrosion control. The above forms of attack are common in the chemical process industry, where Fontana started his career. They

also require water in some form as a part of the environment.

In addition to the above forms of attack, his textbook discusses high-temperature corrosion, corrosion of metals in elevated-temperature gaseous environments.

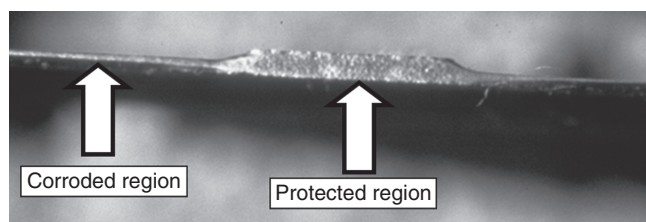
All of the above forms are commonly encountered in oilfield applications and are discussed in some manner in other corrosion textbooks and reference materials.<sup>2-14</sup> Some of the terminology has changed in recent years, and this chapter will attempt to use the terminology most likely to be discussed in oilfield literature.

The end of this chapter discusses forms of corrosion unique to the oilfield environment. It would be possible to discuss most of these oilfield-related terms in discussions of the more universal terminology used in other industries, but it is important to understand the unique circumstances associated with these other forms, or terms, for corrosion.

It is also important to remember that any metal, or metallic system, can have, and usually does have, more than one form of corrosion occurring simultaneously. Successful corrosion control requires that all forms of corrosion likely to occur in a system are addressed.

### GENERAL CORROSION

The term general corrosion is often used instead of the earlier term uniform attack. It is intended to describe situations where the overall surface of a metal undergoes attack. The metal gradually becomes thinner until the structure fails. This attack is seldom uniform in nature, and that is why the earlier term, uniform corrosion, has fallen into disfavor.



**Figure 5.1** Cross section of a carbon steel tray in an amine sweetening unit.<sup>9</sup>

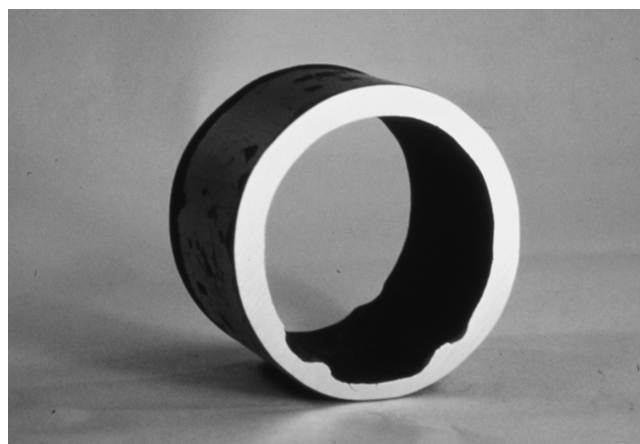
Most general corrosion is localized in nature, but on occasion, uniform attack does occur. Uniform corrosion of carbon steel occurs when the surface is not protected by passive films (formed by reactions of the metal with the environment), scales (deposits of minerals from the environment), or protective coatings. This happens in many acidic environments and can be explained by examination of the potential-pH diagram for iron, Figure 2.11. Figure 5.1 shows uniform corrosion on a tray removed from an amine sweetening unit.

The top center of the photo was protected by a mounting clip and did not corrode. The top side to the left and right was corroded by acidic liquids flowing across the tray, and the bottom of the tray was exposed to acidic vapor condensation and also corroded.<sup>9</sup>

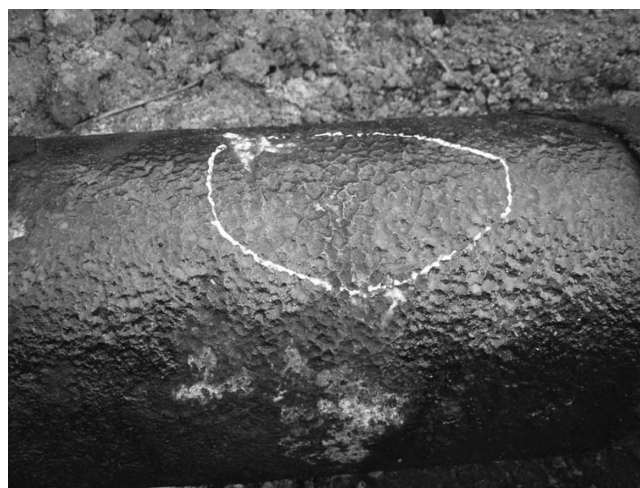
Uniform attack corrosion rates are controlled by the transport of reducible species to the metal surface. This transport results in linear corrosion kinetics; that is, doubling the time of exposure will produce twice the amount of corrosion. Whenever this happens, it is relatively easy to predict corrosion rates based on inspection reports, exposure tests prior to construction, weight loss sampling with corrosion coupons, electrochemical monitoring, and so on.

Unfortunately, most general attack is not uniform, and this can lead to areas of greater and lesser metal loss. This is shown in Figure 5.2, which shows general corrosion along the bottom of a gas well flowline. Similar corrosion patterns are found in condensate return lines of steam systems where air leaks cause the liquid in the lines to become acidic. This corrosion pattern is sometimes termed condensate or CO<sub>2</sub> channeling.

The rippled surface of the pipeline exterior shown in Figure 5.3 is a common appearance for general corrosion. In this case, the corrosion was caused by a debonded coating that led to corrosion by groundwater seeping underneath the debonded coating. Debonded coatings leading to relatively wide areas of general corrosion are a major problem with the pipeline industry. Modern pipeline coatings are much less likely to produce this corrosion pattern.



**Figure 5.2** General corrosion along the bottom of a gas well flowline where acidic condensate thinned the bottom of this horizontal piping. It is obvious that the acidic water flowed at two different levels during the lifetime of this equipment.<sup>9</sup> Photo courtesy NACE International, reproduced with permission.



**Figure 5.3** General attack of pipeline exterior beneath debonded pipeline coating.

General corrosion is the most common form of corrosion and accounts for most of the corrosion experienced worldwide, including upstream oil and gas operations. It is relatively unlikely to be of major technical concern, because it can be monitored and replacements can be planned. It is important to understand when corrosion degradation will be general, or “uniform,” in nature and to understand that most corrosion-associated equipment failures will result from the other forms of corrosion, which tend to be localized in nature.

General corrosion is more likely to occur in locations where acidic water collects. This can be at the bottom



of horizontal piping, as shown in Figures 5.1 and 5.2, but it can also occur in locations where condensation occurs due to thermal gradients. It is important to monitor corrosion rates in the appropriate location, including the bottom of horizontal flowlines and the top of lines where uninhibited condensate can collect.

General corrosion control is normally controlled by design, for example, adding thicker metal corrosion allowances, by including appropriate drainage and inspection capabilities, use of protective coatings or corrosion inhibitors, or by the selection of corrosion-resistant alloys (CRAs). Cathodic protection and modification of the environment, for example, dissolved gas removal, can also be effective.

## GALVANIC CORROSION

Galvanic corrosion can result from electrical contact between two different metals. It can also be caused by any situation that produces changes in electrochemical potential, for example, differences in temperature and chemicals in the environment. In order for galvanic corrosion to occur, the anode and cathode must be in electrical contact and exposed to a continuous electrolytic environments. The most common electrolytic environments are water and wet soil.

### Galvanic Coupling of Two or More Metals

When two corroding metals are electrically connected in the same electrolyte, the more active metal will tend to have more oxidation and corrode at a faster rate while the less active, or noble metal, will have diminished oxidation and corrosion. This is the principle of cathodic protection and of galvanic coatings, for example, zinc coatings or galvanizing, on metal surfaces. Unfortunately, most galvanic couples are between carbon steel, the most common structural metal, and more corrosion-resistant alloys, which tend to be cathodic and to increase the corrosion of the carbon steel. Table 5.1 is based on work by the International Nickel Company at their former seawater laboratory in North Carolina. It shows the relative galvanic relationships between metals and alloys in quiescent seawater at their North Carolina harbor facility. This table is widely cited to indicate the relative potentials of metals in seawater worldwide.<sup>1</sup>

Note that no voltage numbers are indicated on this table. This is because of slight fluctuations in the potential depending on salinity, dissolved oxygen levels, and other seawater variables. The brackets in the table indicate metals that are considered to be galvanically compatible. Many operators have adopted the policy of

**TABLE 5.1 Galvanic Series of Metals and Alloys in Seawater<sup>1</sup>**

↑	Platinum
	Gold
Noble or cathodic	Graphite
	Titanium
	Silver
	Hastelloy C (62Ni, 17Cr, 15Mo)
	18-8 Mo stainless steel (passive)
	18-8 stainless steel (passive)
	Chromium stainless steel 11–30% Cr (passive)
	Inconel (passive) (80Ni, 13Cr, 7Fe)
	Nickel (passive)
	Silver solder
	Monel (70Ni, 30Cu)
	Cupronickels (60-90Cu, 40-10Ni)
	Bronzes (Cu-Si)
	Copper
	Brasses (Cu-Zn)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active)
	18-8 stainless steel (active)
	Ni-resist (high-Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron
	Steel or iron
	2024 Aluminum (4.5Cu, 1.5Mg, 0.6Mn)
Active or anodic	Cadmium
	Commercially pure aluminum (1100)
↓	Zinc
	Magnesium and magnesium alloys

having fluid-handling systems based on stainless steel, copper alloys, titanium alloys, and so on, and try to not mix the alloys in a given process stream whenever possible.

A common example of galvanic corrosion is shown in Figure 5.4, which shows a brass valve connected to galvanized steel piping. The galvanic corrosion on the pipe exterior is obvious.

Control of the water chemistry on the inside is necessary to prevent general corrosion of the galvanized steel, which is seldom galvanized on the pipe interior. The lack of corrosion on the pipe interior emphasizes that all forms of corrosion, to include galvanic corrosion, cannot occur without a chemically reducible species in the environment to consume the electrons liberated by oxidation of the anodic reaction. The lack of reducible species is the main reason why galvanic corrosion is not common in downhole oil well





**Figure 5.4** Galvanic corrosion of galvanized piping in connection with bronze valve.

equipment, where there is little oxygen and other reducible species are unlikely.

### Area Ratio

Whenever two metals are joined in a galvanic couple, the total oxidation reaction, and the consequent corrosion rate, of the anode is increased while the corrosion rate on the cathode is reduced. If the anode is small, then the corrosion will be significantly increased, and this is the reason why many authorities caution that, if galvanic couples cannot be avoided, then the anode must always be the larger component in the galvanic couple. This is the normal situation, because most structures are made from carbon steel, and many connections, for example, instrumentation, tend to be of corrosive-resistant alloys, if only to avoid galling effects on threaded connections.

Figure 5.5 shows the results of galvanic corrosion on a scuba tank. The exterior of the tank is covered with a protective coating and is only wetted for short periods of time. The brass valve does not cause serious corrosion on the carbon steel exterior for two reasons. The time of immersion of a scuba tank is usually very short and is limited by the tank capacity and the energy of the diver. Scuba tanks spend most of their service lives exposed to atmospheric corrosion and relatively little time immersed in seawater or other waters. Even if the tank were immersed for longer periods, the surface area of the valve is relatively small compared to the large tank.

The corrosion of this tank occurred on the interior, where the galvanic couple between the brass valve and the carbon steel tank body involved similar surface



**Figure 5.5** Galvanic corrosion of a scuba tank. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.

areas of wetted metal. Moisture inside scuba tanks collects near the bottom of the tank, and this tank, like many recreational tanks, was not stored in the vertical (valve-up) position that would have kept the liquid condensate at the bottom of the tank. Bimetallic galvanic corrosion led to enough wall thinning to produce rupture due to internal corrosion.

The area ratio concept must be used with caution and a careful consideration of the structures involved. It is important to always avoid accelerated corrosion on the critical component, the one that, if it corrodes, will lead to system failure.

**Weld Filler Metals** Filler metals for welding should always be cathodic to the base metals being joined. Welds are used for immersion and atmospheric exposure, and in either situation, the most critical location in the galvanic couple is the weld and adjacent area. The filler metal should always be cathodic to the base metal being joined.

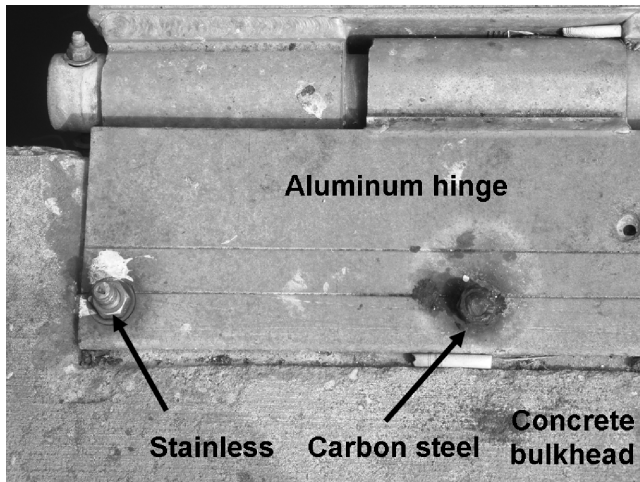
**Fasteners** Unlike welded connections, threaded connections should seldom be used in immersion environments. They are usually exposed to atmospheric corrosion. It is not unusual for engineers to avoid



**Figure 5.6** Corrosion of carbon steel structure connected to stainless steel fasteners.



**Figure 5.8** CRA fasteners on flange connecting carbon steel piping to CRA piping.



**Figure 5.7** Aluminum hinge connected to concrete bulkhead with stainless and carbon steel fasteners.

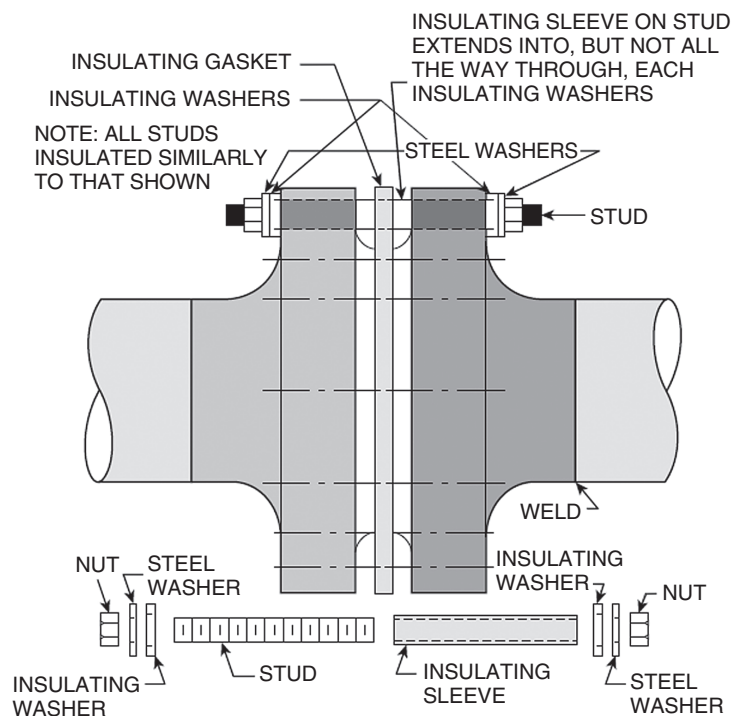
specifying corrosion-resistant fasteners because the most common corrosion-resistant fasteners have anodic coatings, usually zinc or cadmium, and the concern is that the small fastener will be connected to a large carbon steel structure. This is a misguided caution. The fastener is the critical component in these applications, and failure of the fastener is to be avoided if at all possible. In addition, these very thin metallic coatings are only appropriate for atmospheric exposure and the wetted area around a fastener is usually very small, limiting the effect of the “large anode.”

Figures 5.6 and 5.7 show two different structures with threaded connections leading to corrosion. In Figure 5.6, a galvanized carbon steel pipe support is connected to a concrete pad with stainless steel fasteners. The galvanizing is almost gone from the carbon steel, and

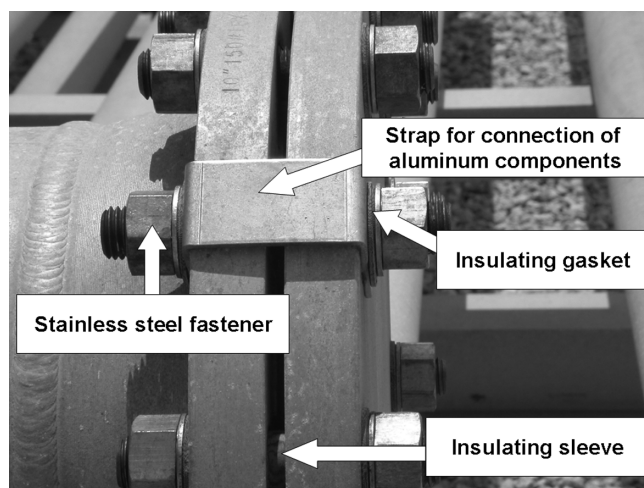
the corrosion of the carbon steel at the carbon steel–stainless steel interface is obvious. Even though the carbon steel has corroded, the structure is in no danger of failing. The situation is different on the aluminum hinge shown in Figure 5.7. In this case, the formerly galvanized carbon steel fastener is corroding, and the adjacent aluminum-to-stainless steel connection shows minimal signs of deterioration. The inherent corrosion resistance of aluminum in a marine atmosphere means that the aluminum is protected by a passive film, and the effects of joining it to stainless steel are minimal. The supposedly more compatible aluminum-zinc galvanic couple on the galvanized carbon steel fastener was ineffective. The thin zinc coating did not last very long in a marine atmosphere, and the carbon steel fastener is corroding and will eventually fail.

Galvanic corrosion with threaded fasteners can be avoided. Figure 5.8 shows a connection between a carbon steel piping and CRA piping. CRA fasteners are used at the flanges. No increased corrosion of the carbon steel pipe due to the connection has occurred. All of the apparent corrosion is due to coating defects. The reason that no galvanic corrosion has occurred is because the two metals are electrically insulated. CRA-threaded connections are routinely insulated from carbon steel pipes using electrical insulation kits like those shown in Figure 5.9. These kits include reinforced gaskets to separate the fasteners from the metal being connected and sleeves that fit around the shank of the fastener from the flanges. This is shown in Figure 5.10. Electrical isolation supplies are routinely available from many piping and corrosion control suppliers.

Once an insulation kit has been installed, it is important to check against electrical continuity using a simple



**Figure 5.9** Insulated flange assembly.<sup>15</sup> Photo courtesy of NACE International, reproduced with permission.



**Figure 5.10** Electrical isolation of aluminum piping from stainless steel fasteners.



**Figure 5.11** Continuity testing to be sure that electrical isolation has been achieved. Photo courtesy S. Munoz, Corrosion y Proteccion, Cuernavaca, Mexico.

ohmmeter. This is shown in Figure 5.11. It is important to use reinforced gaskets in these insulation installations, because non-reinforced insulators may creep and cause electrical shorting. It is also important to periodically check these insulated joints because they can become shorted due to motion between piping components.

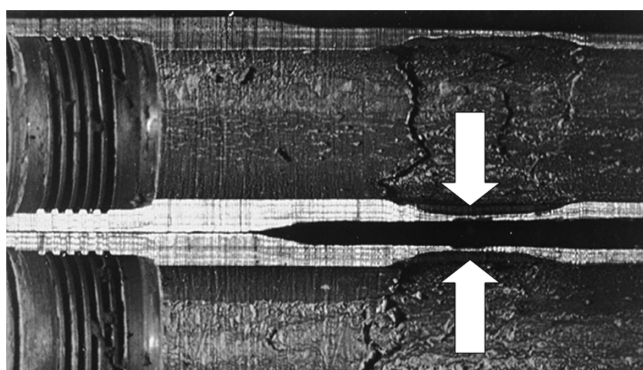
**Metallurgically Induced Galvanic Corrosion** There are a number of metallurgically induced corrosion cells possible. This discussion mentions a few that have been reported in oilfield environments.

**Heat-Affected Zone (HAZ) Corrosion** Welding produces changes in metallurgical structure. The idea that





**Figure 5.12** Heat-affected-zone corrosion on carbon steel crude oil pipeline.



**Figure 5.13** Ringworm corrosion in oilfield production tubing. Note the internal corrosion in the heat-affected zone a short distance from the welded connection.

filler metals should always be cathodic to the base metal being joined has already been discussed in the discussion of the area effect. Unfortunately, improper welding procedures can produce situations where the HAZs become anodic to the surrounding metal. This is shown in Figure 5.12, which shows HAZ corrosion in a crude oil pipeline. Note how the corrosion is located parallel to the field-installed girth weld and no corrosion is associated with the longitudinal weld that was made under controlled conditions in the pipe mill.

Problems with girth welds are common, and this is why pipeline inspections, for example, internal pig inspections, concentrate on these areas as potential corrosion sites. Many organizations have also decided not to use electrical-resistance-welded (ERW) oil country tubular goods (OCTGs) because of corrosion problems along the longitudinal welds.

**Ringworm Corrosion** Figure 5.13 shows a phenomenon called “ringworm corrosion,” which was a major corrosion concern in the Permian Basin of West Texas

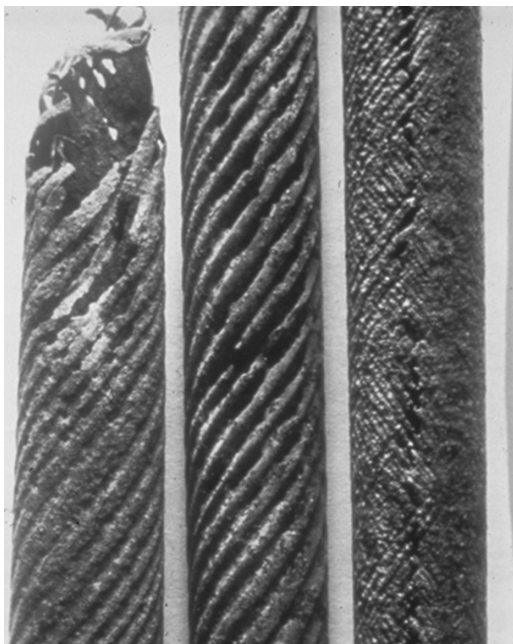
in the 1940s and early 1950s. The metal in the HAZ of oilfield production tubing sometimes corrodes near the upset head or welded tool joint. In upset tubing, the metal needs to be heated to the austenite stable region (above approximately 750°C (1382°F) so that it can be deformed. Welded connections have similar HAZs that can lead to the same problem.<sup>9,16</sup> The problem was solved in the 1950s by introducing the practice of full-length normalizing—heat-treating the entire joint to a suitable (austenizing) temperature and then air-cooling (normal cooling procedure) so that the entire joint has the same microstructure and corrosion resistance. This problem has reappeared worldwide in recent years, because engineers and purchasing organizations have not learned the lessons of decades past.

**Lüders Band Corrosion** Lüders bands (also called stretcher marks, Hartmann lines, or Piobert lines) are localized bands of plastic deformation that can occur on carbon steels and other materials in regions of localized plastic deformation.<sup>17</sup> They form in carbon steel and other materials when the initial resistance to deformation is overcome and localized yielding (plastic deformation) occurs. This localized deformation is usually at approximately 45 degrees to the primary stress axis and may form ripples, Lüders bands, when the deformation reaches the metal surface. These deformations are an indication that part of the metal has been stressed more than the other regions, which are in a lower energy state and are less susceptible to corrosion. If the differences in stress are not removed, they can lead to a corrosion pattern termed “Luders band” corrosion. This is shown in Figures 5.14 and 5.15. Once again, full-length normalizing is the recommended solution to this problem. While Figures 5.14 and 5.15 show downhole tubing; this is also a potential problem on pipeline steel.

While the corrosion patterns shown in Figures 5.14 and 5.15 are due to plastic deformation during pipe-mill processing, this problem can also occur as a result of deformation in the field. It is important that piping, especially for large-diameter pipelines, be handled and bent very carefully to avoid localized regions of high stress and the formation of Luders bands.<sup>18–20</sup>

### **Environmentally Induced Galvanic Corrosion**

Changes in electrolytes produce galvanic corrosion cells. Typical examples are the differences between the potentials in deep water, which is usually colder and has less oxygen, and surface water, which is high in oxygen. Galvanic differences also occur offshore from major rivers, where the surface water may be fresh and have low salinity for several meters before the lower, denser saltwater becomes prevalent. Temperature gradients



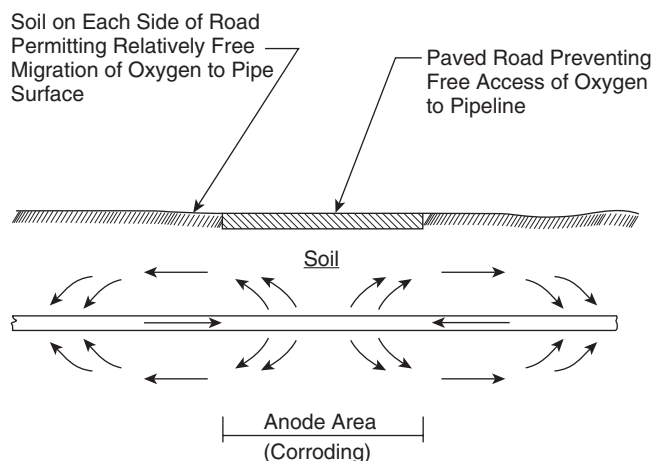
**Figure 5.14** Lüders band corrosion on oilfield production tubing.



**Figure 5.15** Close-up view of Lüders band corrosion on OCTG.

can also cause changes in potential. The reasons for these potential differences are easy to explain based on the principles of the Nernst equation. Most oilfield environments, for example, wet soil or brackish water, are too complex to model using the Nernst equation, and field measurements are necessary to confirm the presence of these potential gradients, which are often termed concentration cells.<sup>2</sup>

The following examples are important in onshore pipelines and similar situations.

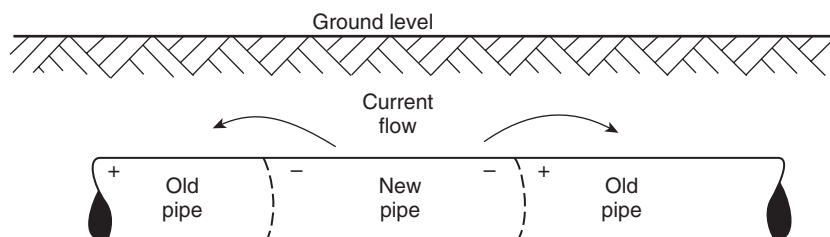


**Figure 5.16** Differential aeration cell on a pipeline beneath a paved road.<sup>21</sup> Figure courtesy of NACE International, reproduced with permission.

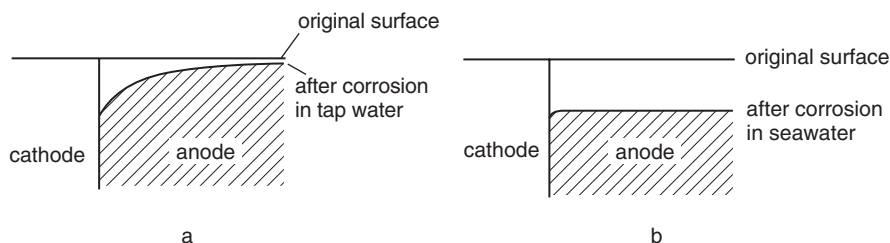
*Pipeline under Road Crossing* This is an obvious situation where the moisture, access of air, and soil compaction levels can combine to produce differences in corrosive environments underneath roads or similar moisture and permeation barriers and the land on either side of the road. This is shown in Figure 5.16, which indicates that the relatively high oxygen rates adjacent to the roadway lead to anodic corrosion beneath the pavement. While this is a common situation, it is also possible in certain climates that pipelines beneath roadways and other moisture permeation areas may be less corroded than the wetter areas nearby. Because it is hard to predict the complex effects of differential environments at road crossings, it is considered good practice to monitor pipeline potentials or to use other means of monitoring corrosion at road crossings.

*Old Pipe Connected to New Pipe* New sections of pipe in an old pipeline are often anodic to the older pipe, either because the old pipe is covered with heavy layers of rust that are cathodic to the new pipe or because the new pipe is placed in a more aggressive environment. One of the reasons for placing a new pipe, as shown in Figure 5.17, is as a repair of corroded pipe. This is an indication that the environment where the repair is located is more corrosive than nearby areas. Even if that were not the case, for example, when the new pipe is the result of a modification, that is, placing a new connection to an existing line, the new pipe is likely to be located in less compacted soil which is more permeable to water and air. Some organizations have adopted the policy that whenever a new pipe installation occurs, they will install galvanic anodes in the location. The cost of the anode is minimal compared with the cost of the construction, and it may help and cannot hurt.





**Figure 5.17** New pipe connected to old pipe producing a galvanic corrosion cell.<sup>9</sup>



**Figure 5.18** Effect of electrolyte conductivity on the distribution of galvanic corrosion.<sup>22</sup>

### Polarity Reversal

Zinc-coated steel (galvanized steel) is used for corrosion control in atmospheric exposures and in freshwater. It was reported in 1939 that zinc sometimes becomes cathodic to carbon steel in freshwater at elevated temperatures. This caused concern in a number of circles and changed engineering practice, for example, the construction of domestic hot water heaters. The reversal occurs in some freshwaters at temperatures above 60°C (140°F). Research in the 1950s indicated that this polarity reversal, where galvanized steel suffers accelerated attack, occurs in waters high in carbonates and nitrates but is unlikely to occur in waters with chlorides and sulfates, such as seawater or formation water.<sup>2,22–23</sup> The only other commercially important polarity reversal is with tin plating. Tin cans have an anodic coating (the tin) in deaerated organic acids (food containers), but this relationship reverses upon exposure to air, and tin acts like a noble coating.

Many authorities advise designers to check the polarity of metals in electrolytes of interest but, as a practical matter, virtually all corrosion-related designers assume that the potentials shown in Table 5.1 are valid, and testing to determine relative galvanic relationships, while possible, is rarely done.

### Conductivity of the Electrolyte

Figure 5.18 shows how galvanic corrosion is concentrated near the two-metal interface in tap water while it extends for a long distance in seawater. At one time,

a “rule of thumb” used in seawater stated that galvanic corrosion effects would only extend approximately 10 pipe diameters into seawater heat exchangers.<sup>24</sup> Later research at the Ocean City Research Laboratory showed that the effects of changing the header material on seawater-cooled heat exchangers extended much farther than previously thought.

### Control of Galvanic Corrosion

The obvious way to control galvanic corrosion is to avoid the use of different alloy systems in the same electrolyte. Oil companies follow this guideline by not mixing alloy families in process streams, for example, using only aluminum, copper, stainless steel, or carbon steel whenever possible.

Dielectric (insulating) connections, like those shown in Figures 5.9–5.11, are effective means of preventing galvanic corrosion on atmospherically exposed flanged connections. This is especially important when connecting aluminum piping, as shown in Figure 5.10, because non-galling aluminum fasteners are not available. As stated above, it is generally inadvisable to use bolted connections on submerged or buried piping systems. Dielectric unions along piping systems are often overcome by electrical grounding, and this is a further reason to not mix alloys whenever possible.

One seldom-discussed option is the use of “sacrificial” nipples in piping systems where galvanic corrosion will occur, for example, between galvanized piping and CRA valves. A short, easily removed nipple removes



**Figure 5.19** Pitting corrosion on carbon steel potable water pipe. Note the deepest pit at the 2 o'clock position on this 100mm (4 inch) pipe.

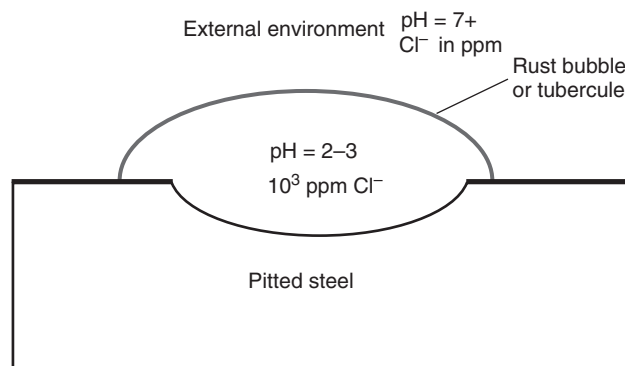
the need for welding when replacing the corroded carbon steel nearest to the CRA.

When connections of two incompatible metals are unavoidable, it is important that the smallest (or thinnest in the case of heat exchanger tubing) metal must be cathodic to the surrounding metals. Cathodic protection of unavoidable two-metal contacts is also possible.<sup>25</sup>

## PITTING CORROSION

Pitting corrosion can be defined as localized attack on a metal surface in locations where the overall metal surface is relatively uncorroded and is often covered with passive films or scales. Figure 5.19 shows typical pitting on a potable water pipe. Note the deepest pit in the 2 o'clock position and the large rust bubbles or “tubercles” that have formed over the pits. It is common that the rust tubercles can impede water flow and may be more significant than the relatively shallow (compared with the size of the tubercles that form over them). These tubercles are porous corrosion products with scale deposits and can prevent access of corrosion inhibitors or biocides to the metal substrates. The most common way of removing deposits like shown in this picture is by mechanical removal using pipeline pigs or similar devices.

Pitting corrosion is perhaps the most common form of oilfield corrosion after general attack. Unlike general attack, which can be monitored and predicted, pitting corrosion may start and propagate quickly in relatively short time periods, leading to significant damage.



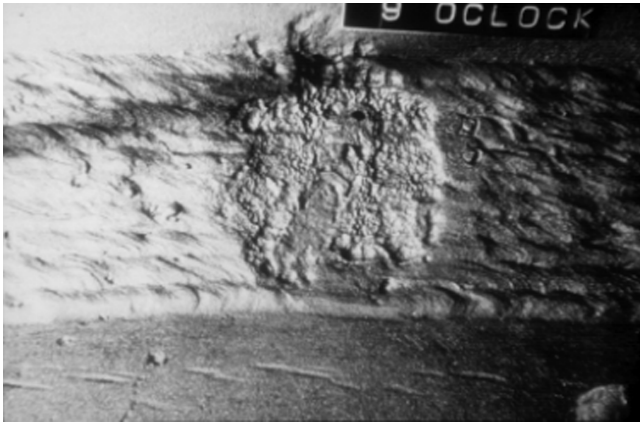
**Figure 5.20** Pit with pH and chloride concentration changes indicated.<sup>27</sup>

Monitoring for pitting corrosion requires frequent inspection or sampling, because no corrosion may occur for a long time followed by relatively aggressive pit initiation and growth.

## Occluded Cell Corrosion

Pitting is only one of several forms of corrosion that have similar mechanisms. In 1970, B. F. Brown suggested the term “occluded cell corrosion” to encompass the mechanisms of pitting, crevice, stress corrosion, intergranular corrosion, filiform corrosion, and exfoliation.<sup>26</sup> He also suggested that corrosion fatigue, which shares several characteristics with the other forms of corrosion, had enough unique characteristics that it should be considered separately. Since this suggestion in 1970, many researchers have confirmed Brown’s suggestions that all of these forms of corrosion shared several characteristics, including acidification near the corroding anode and concentration of halides, usually chloride ions in the corroding location. Figure 5.20 summarizes the results of research in many worldwide laboratories.

Note that the pH of the bulk environment, tap water, is indicated to be slightly basic ( $\text{pH} > 7$ ). This is common for potable water supplies worldwide, because it was learned in the 1920s that high-pH water would produce calcium carbonate scales that retard corrosion in freshwater.<sup>2</sup> The pH inside the rust bubble or tubercle is shown to be between 2 and 3. This is a commonly reported pH for most occluded cell corrosion, although pHs below 1 have also been reported.<sup>28</sup> The low pH is a result of oxidation. All oxidation reactions lower the pH of the environment, just as all reduction reactions increase the pH. The high concentration of chlorides is due to the rapid migration of negatively charged anions, of which chlorides are the most common, to balance the electrical charge in the local low-pH environment inside



**Figure 5.21** Corrosion pit on a weld of an offshore platform. The overlying marine growth and tubercles were mechanically removed to allow visual inspection using a remotely operated vehicle (ROV) with a television camera.<sup>29</sup>

the rust bubble or tubercule. Similar changes in pH and chloride levels have been reported in virtually all examples of occluded cell corrosion as well as in fatigue cracks, which are now considered to be occluded cells by many researchers. The combination of low pH and increased chloride levels inside occluded cells means that, once this form of corrosion starts, it is likely to proceed at an accelerated rate.

Removal of occlusions, for example, mechanical removal of the rust bubble or tubercule, can slow or stop pitting corrosion, and this is a reason for pipeline pigging and other mechanical means of cleaning piping systems.

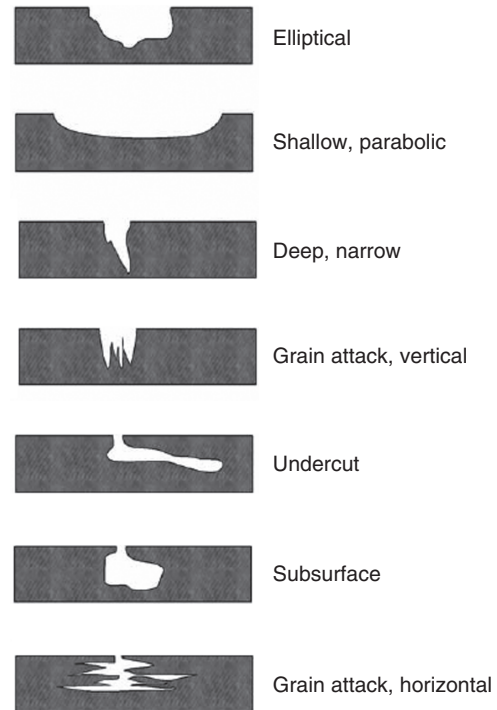
Figures 5.19 and 5.20 show pitting corrosion on carbon steel. Other alloys may not form rust bubbles or tubercles, but they all have low pHs and concentrated halides (chloride, bromide, etc.) inside the pits.

### Pitting Corrosion Geometry and Stress Concentration

Many corrosion pits, like those shown in Figures 5.19 and 5.20 are relatively shallow, but they can still serve as stress concentrators that initiate stress corrosion cracking (SCC) or corrosion fatigue.

The stress concentration and loss of cross section caused by the pit shown in Figure 5.21 was considered severe enough that it could have led to corrosion fatigue of the North Sea platform where it was found. The pit in question was repaired by welding using underwater divers.<sup>29</sup> Shortly after the publication of Figure 5.21, another North Sea platform collapsed due to corrosion fatigue with many fatalities.<sup>30</sup>

Other pits can have different geometries as shown in Figures 5.22 and 5.23. Film-protected alloys are more likely to form pits with relatively small surfaces and



**Figure 5.22** Pit morphology.<sup>31</sup>



**Figure 5.23** Pitting on stainless steel tubing.<sup>32</sup>

widespread corrosion beneath the pit entrance, but environmental factors, for example, scale deposits or biofilms, can also produce similar pitting patterns in carbon steel.

### Pitting Initiation

Pits form at defects on metal surfaces. These are often microscopic in nature and cannot be detected by field-level inspection devices. Examples of pit initiation sites include impurities or grain boundaries on the metal



**Figure 5.24** Pitting corrosion of an Alloy 825 (UNS N08825) heat exchanger baffle exposed to seawater.<sup>28</sup>

surface and mechanical damage to surface films, either passive films or scales.<sup>4</sup>

### Pitting Resistance Equivalent Numbers (PRENs)

There are a number of published PRENs. The most commonly used PREN is from NACE (formerly the National Association of Corrosion Engineers) RP0176/ISO 15156:<sup>33</sup>

$$\text{PREN} = w_{\text{Cr}} + 3.3(w_{\text{Mo}} + 0.5 w_{\text{W}}) + 16w_{\text{N}}$$

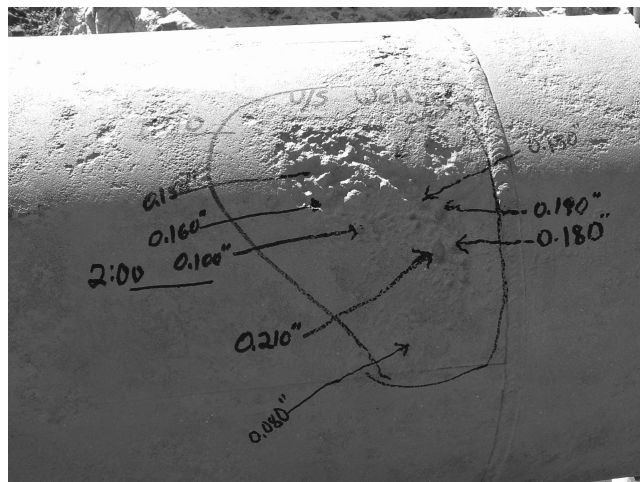
where:

- $w_{\text{Cr}}$  is the weight percentage of chromium in the alloy;
- $w_{\text{Mo}}$  is the weight percentage of molybdenum in the alloy;
- $w_{\text{W}}$  is the weight percentage of tungsten in the alloy;
- $w_{\text{N}}$  is the weight percentage of nitrogen in the alloy.

Larger values of PREN are considered to indicate greater resistance to pitting corrosion. A more complete discussion of PRENs is available in Chapter 4, Materials.

While PREN numbers can be used to compare the supposed resistance of different alloy groups to pitting, they offer only general guidelines on pitting and crevice corrosion resistance and do not consider all alloying constituents, for example, nickel, that contribute to localized corrosion resistance.

Figure 5.24 shows deep pitting within months, of a plate composed of Alloy 825 (UNS N08825), an alloy with a PREN in the low 30s. It would normally be considered a very corrosion-resistant alloy. Even the most corrosion-resistant alloys are subject to pitting and crevice corrosion in elevated-temperature brines like seawater or formation waters.



**Figure 5.25** Pitting on carbon steel pipeline at a location where shrink sleeve protection of a girth weld was ineffective. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

### Statistics

Figure 5.25 shows the distribution of pits on a pipeline where a shrink sleeve coating of a girth weld was ineffective. The markings on the pipe indicate that the deepest pits vary from 0.100 in (2.5 mm) to 0.210 in (5.3 mm) in depth. This is a more than 100% variation in pit depth, and most of the exposed surface in this location is relatively uncorroded. The wide variability in pit depths was the subject of an early study of pipeline pitting by Gordon Scott, an American Petroleum Institute (API) fellow and later NACE president working at the National Bureau of Standards.<sup>34</sup> The conclusions from this study, which involved excavation of miles of pipeline in several states, can be summarized as follows:

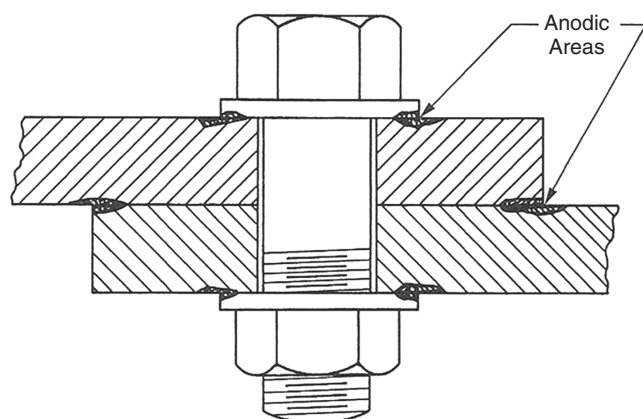
- The larger the number of pits, the deeper the maximum pit.
- Larger areas of inspection will produce deeper maximum pit depths.

These results from some of the earliest scientific research into pipeline corrosion indicate that small samples of any type, whether coupons used to monitor corrosion control effectiveness or limited inspections of pipeline exteriors using External Corrosion Direct Assessment (ECDA) methods, are unlikely to identify the deepest pits in any real system.<sup>35</sup>

### Prevention of Pitting Corrosion

Pitting corrosion on carbon steels is minimized by the use of cathodic protection, protective coatings, and





**Figure 5.26** Crevice corrosion locations on a bolted connection.<sup>36</sup>

corrosion inhibitors. The same approach is applied for martensitic stainless steels (13Cr alloys) used as OCTGs. Other CRAs have varying pitting and crevice corrosion resistances. Stainless steels and similar alloys benefit from the addition of molybdenum (e.g., UNS S30400 is more susceptible than UNS 31600). Titanium alloys are generally considered to be immune to pitting corrosion, but palladium or molybdenum additions are found to be helpful in adding resistance at elevated temperatures.

## CREVICE CORROSION

The mechanisms of crevice corrosion are essentially the same as for pitting corrosion; the only important difference is that the crevice, which serves as the corrosion site, is readily visible to the unaided eye.

Figure 5.26 shows locations of crevice corrosion susceptibility on a bolted connection. Problems with crevice corrosion are a major reason why bolted connections are seldom used in submerged applications, although cathodic protection to minimize crevice corrosion is possible.<sup>25</sup> Bolts also suffer crevice corrosion as shown in Figure 5.27. The 10-year-old carbon steel bolt on the right in Figure 5.27 was installed on a valve in a water system.

Heat exchangers are another type of equipment with significant crevice corrosion problems. The corrosion of a header plate is shown in Figure 5.28. Heat exchanger tubing, which is much thinner than header plates and the shells, is another part of heat exchangers subject to both crevice corrosion and to pitting.

Corrosion can occur under many types of crevices. The corrosion shown in Figure 5.29, which was revealed when the pipeline moved and the underlying pipe was



**Figure 5.27** Crevice corrosion of a 10-year-old bolt on a water-control valve.<sup>37</sup>



**Figure 5.28** Crevice corrosion on a heat exchanger header plate.

exposed, is also considered to be crevice corrosion. This kind of corrosion also occurs in many areas where piping and supports are connected and are made worse by relative movement between the two materials.

Crevice corrosion is also called underdeposit attack and has a variety of other names as well. The corrosion in the 6 o'clock position on the cupronickel firewater line shown in Figure 4.31 is an example of underdeposit crevice corrosion in a Gulf of Mexico firewater system. Many microbially influenced corrosion (MIC) situations could also be described as underdeposit attack, although they are most often termed MIC-related pitting.

Many authorities describe crevice corrosion in terms of electrochemical concentration cell corrosion.<sup>2,4</sup> The electrochemical potential differences between inside a





**Figure 5.29** Crevice corrosion underneath the restraining strap on a pipeline. Photo courtesy of J. Byrd, Byrd Coating Consultants, Wellington, Florida.

crevice and outside a crevice can be described as oxygen concentration cells and metal ion concentration cells. The relatively high oxygen concentrations available for reduction outside a crevice are used to explain why oxygen concentration cells cause crevice corrosion inside a crevice. The Nernst equation can also be used to explain how high metallic ion concentrations inside a crevice would lead to metal ion concentration corrosion immediately adjacent to the edge of the crevice. While this is an interesting possibility, metal ion concentration cell crevice corrosion has never been reported outside the laboratory.

Crevice corrosion is usually, but not always, a topside problem.<sup>38</sup> Leaking gaskets, mechanical motion leading to openings in bolted connections, and a variety of other sources of moisture ingress produce corrosive conditions inside crevices. The chemistry of the electrolyte inside a crevice is typical of all occluded cells, and increasing metal ion concentrations, reduced pHs, and the migration of chloride and other negatively charged anions all contribute to the corrosivity inside the crevice. Relatively high oxygen concentrations lead to accelerated attack, because oxidation must be balanced by nearby reduction reactions. This is the reason why crevice corrosion is usually minimal in downhole environments. Complicated geometries, for example, on pumps, are common downhole, but the lack of a reducible species in many oil wells prevents corrosion. Unfortunately, gas wells, which are acidic and corrosive, can have crevice corrosion, and the use of CRAs frequently becomes necessary on wellhead equipment and other complicated surfaces exposed to corrosive condensates.<sup>39</sup>



**Figure 5.30** Crevice corrosion of a titanium alloy flange. Photo courtesy of NACE Basic Corrosion course, reproduced with permission.

### Alloy Selection

Crevice corrosion can be a problem on a wide range of alloys. Molybdenum additions are often used to increase the pitting and crevice corrosion resistance of stainless steel tubing. Type 316 (UNS S31600) is a standard grade often specified instead of the similarly available Type 304 (UNS S30400) for most marine atmospheric applications, and higher alloy grades are also available at increased costs.

It is important to always specify the correct alloy to control crevice corrosion. Titanium, which is considered immune to crevice corrosion in ambient temperature seawater, may corrode at elevated temperatures. Titanium alloys with palladium, molybdenum, or ruthenium additions are more resistant to crevice corrosion. Figure 5.30 shows crevice corrosion of a titanium flange. The engineers specified titanium, but did not specify the alloy, so the organization installed a commercially available Ti-6Al-4V (UNS R56400) part in seawater service. This particular application, which was not at elevated temperatures, could have used commercially pure titanium (ASTM Grades 1–4) which would have worked quite well. The same major oil company now uses palladium additions (ASTM Grades 7 or 11) on all applications to avoid any possibility of crevice corrosion.

### Filiform Corrosion

Filiform corrosion (filamentary corrosion underneath protective coatings on metal surfaces) is a special type of crevice corrosion. The long, thin filaments of corrosion products extend through defects in the protective coating and provide galvanic contact between the



**Figure 5.31** Filiform corrosion underneath a transparent protective coating. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.

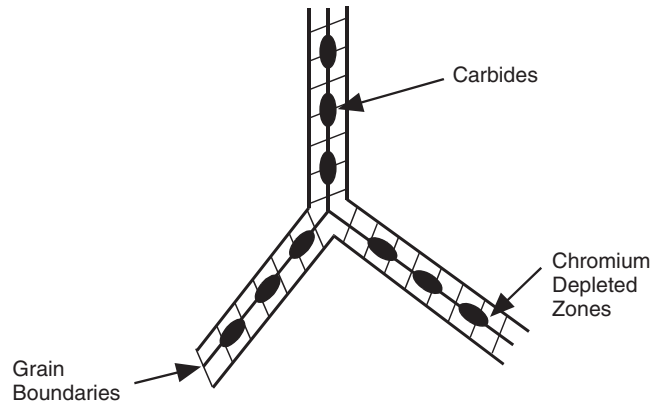
oxygen-deficient anode near the metal-coating interface and the relatively high-oxygen environment outside the coating. This is shown in Figure 5.31. While Figure 5.31 shows filiform corrosion underneath a thin transparent coating, it also occurs underneath many other protective coatings. The corrosion starts at coating defects, typically along edges, and proceeds underneath the coating. It may eventually lead to coating disbonding and further extensive corrosion of the metal substrate.

## INTERGRANULAR CORROSION

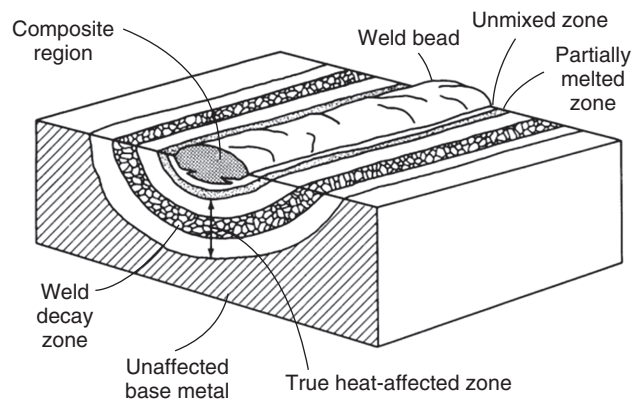
Most grain boundaries are more reactive than the surrounding base metal due to the presence of impurities and other defects. The increased reactivity of grain boundaries over crystal matrices is usually negligible and is of minimal consequence. Intergranular corrosion occurs when significant differences in alloy chemistry near grain boundaries cause significant attack and the alloy disintegrates. Intergranular corrosion can be a significant problem in stainless steels and in some aluminum alloys. Other alloy systems, for example, highly alloyed austenitic iron-chromium-nickel alloys, can also have this problem.

### Stainless Steels

Most upstream intergranular corrosion of stainless steels is due to improper welding practices. The temperatures involved in welding create HAZs where carbon in the stainless steel can react with chromium



**Figure 5.32** Sensitized regions in austenitic stainless steel.



**Figure 5.33** Heat-affected zones in welded stainless steel.<sup>40</sup> Reprinted with permission of ASM International. All rights reserved, <http://www.asminternational.org>.

to form chromium carbides. This is most likely to happen in grain boundaries, where carbon is most likely to be concentrated. The result is chromium depletion from the surrounding grain boundary regions and the creation of three composition ranges in the metal:

- Chromium carbides concentrated in the grain boundaries
- Chromium-depleted zones in the grain boundary regions
- Bulk crystals with no segregation and the overall composition of the alloy

This is shown in Figure 5.32, which is common to virtually all corrosion engineering textbooks.

The continuous chromium-depleted regions are anodic to the larger unaffected grains and this unfavorable area ratio causes increased corrosion in the grain boundaries. The HAZs are shown in Figure 5.33. Note

that the newly recrystallized grains are located approximately halfway through the HAZ.

This corrosion can be minimized by using austenitic stainless steels with lower carbon contents, 304L or 316L (UNS S30403 or UNS S 31603), or by using stabilized grades of stainless steel, types 321 or 347 (UNS S32100 or S34700), which have titanium or niobium additions. The titanium or niobium additions are added as “carbide getters” that preferentially form titanium or niobium carbides, thus tying up the carbon and minimizing the formation of chromium carbides. Both of the above approaches are similarly effective in minimizing sensitization and the resulting intergranular weld decay in HAZs of austenitic stainless steels. North American steel producers tend to prefer the low-carbon approach, and European producers have traditionally preferred the stabilizing addition approach.

Manufacturing operations can undo sensitization by post-weld heat treatment, but this is very difficult in field operations.

Once again, the use of carefully approved welding procedures is very important.

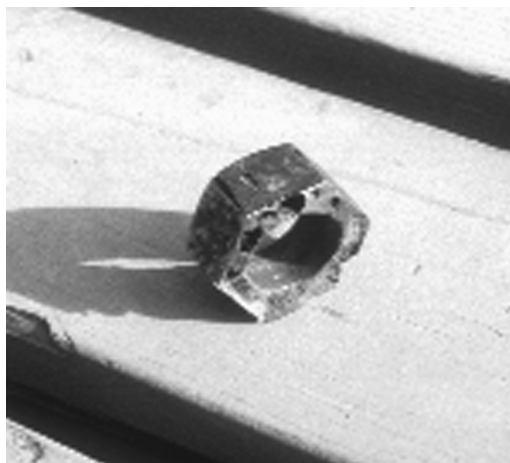
Refineries and other high-temperature operations can sometimes operate at temperatures above 500°C (950°F) where sensitization can occur. Most downstream operations are at temperatures too low for this to happen, but it is possible for manufacturers to deliver sensitized stainless steel components due to improper manufacturing procedures.

### Corrosion Parallel to Forming Directions

Many metal objects are more prone to corrosion on surfaces perpendicular to the metal forming direction (the rolling or drawing direction). This is shown in Figure 5.34, which shows a stainless steel nut that corroded along grain boundaries in a marine exposure. The nut was machined from hexagonal bar stock, and sulfide stringers parallel to the original bar stock’s longitudinal direction allowed intergranular crevice corrosion on the facing side (to the right in the picture) of the nut. Most machining-grade metals have deliberate additions of a soft second phase to expedite machining processes. Sheet, plate, and tubing are also more corrosion susceptible in the through-thickness direction. This is why corrosion rates are faster on cut surfaces, for example, where tapping is necessary for instrumentation connections. No inappropriate heating was involved in causing the corrosion shown in Figure 5.34.

### Aluminum

Aluminum alloys get their strength from alloying. This makes the grain boundaries of aluminum susceptible to



**Figure 5.34** Intergranular corrosion along the forming direction on a stainless steel nut.



**Figure 5.35** Exfoliation of aluminum at a coastal location.

corrosion, and the formation of aluminum oxide pushes the metal apart in a direction perpendicular to the rolling direction. This is shown in Figure 5.35, which shows exfoliation (the loss of leaves) intergranular corrosion of an aluminum guard rail in a coastal marine environment. Note how the galvanized bolt has rubbed against the bolt hole on the aluminum rail and caused corrosion where the bare metal was exposed after the protective aluminum oxide passive film was removed. This picture is also an example of the problems associated with improper design for thermal expansion and contraction, which caused the relative motion between the expanding and contracting aluminum and the fixed bolt location. This problem of expansion and contraction can be expected to occur on helidecks and other sunlight-exposed structures. Aluminum is not welded in most field applications, so exposure of



through-thickness grain boundaries at bolted connections is common.

### Other Alloys

Carbon steel and other alloys can also suffer grain boundary attack and exhibit exfoliation, but welded stainless steels and aluminum exposed to wet atmospheres are the most likely alloys to have this problem in the oil field. All metals are especially prone to this form of corrosion on surfaces perpendicular to the forming direction, where the grain boundaries are closer.

## DEALLOYING

Dealloying is a corrosion process where one constituent of an alloy is removed, leaving an altered residual structure. It was first reported in 1886 on copper-zinc alloys (brasses) and has since been reported on virtually all copper alloys as well as on cast irons and many other alloy systems.<sup>1,2</sup> Alternate terms for dealloying include parting, selective leaching, and selective attack. Terms such as dezincification, dealuminification, and denickelification indicate the loss of one constituent of the alloy, but the general term dealloying has gained wider use in recent years.

Figure 5.36 shows a typical example of dealloying. The chrome-plated brass valve corroded at breaks in the coating. The dark regions on the brass are regions where virtually all of the zinc has been removed, leaving a porous copper structure with virtually no mechanical strength and no change in surface profile.

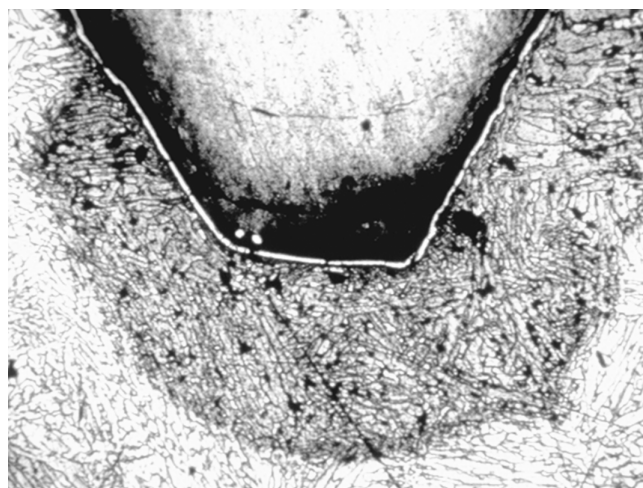
Dealloying is also a problem with cast irons. While both diffusion and noble metal deposition are discussed as mechanisms associated with dealloying in copper-based alloys, the mechanism of dealloying in cast irons involves the dissolution of the iron-rich phases, leaving a porous matrix of graphite and iron corrosion products. Figure 5.37 shows a porous graphite plug in a cast iron water pipe.

### Mechanism

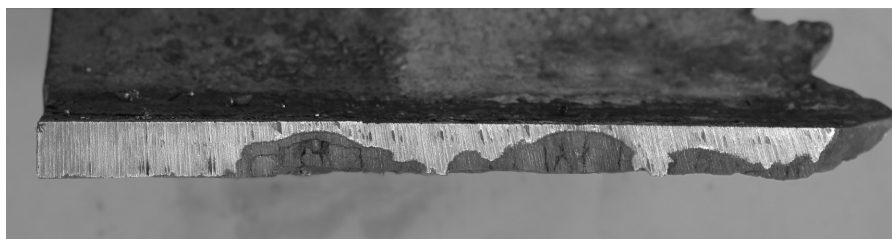
Dealloying has been shown to occur by at least two different mechanisms. Sometimes, the entire alloy dissolves, and one constituent redeposits on the corroded metal surface. In other circumstances, diffusion removes only the more corrosion-susceptible constituent, leaving an altered porous matrix. Both mechanisms have been shown to occur simultaneously on the same metal surface.<sup>41</sup>

### Selective Phase Attack

Selective phase attack is a form of dealloying where some phases of an alloy are more corrosion susceptible than the overall alloy. It is an oilfield problem with large bronze castings. The cross section of a nickel-aluminum-bronze pump component is shown in Figure 5.38. The problem is caused by improper foundry procedures that produce susceptible phases in otherwise corrosion- and erosion-resistant alloys used for large seawater pumps. Quality control checks on bronze castings need to



**Figure 5.36** Dezincification of a chrome-plated scuba tank valve.<sup>41</sup>



**Figure 5.37** Dark, graphitic corrosion on the exterior of a cast iron water main. Photo courtesy of Testlabs International, Ltd., Winnipeg, Canada, <http://www.testlabs.ca>.



include chemical analysis to insure that the composition is within specifications.<sup>43</sup>

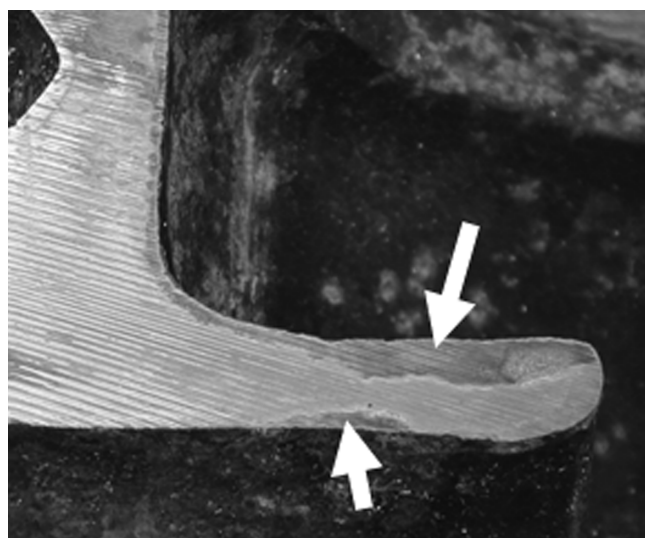
### Susceptible Alloys

Virtually all copper-based alloys are susceptible to dealloying. Stagnant seawater is more corrosive and can produce dealloying even in cupronickels, which are generally quite corrosion resistant. (Figure 5.39).<sup>44</sup>

Cast irons are also susceptible. Ductile cast iron is less susceptible, but it is not immune.

### Control

Dealloying is normally controlled by alloy selection. Cupronickels, while not immune, are probably the best



**Figure 5.38** Selective phase attack of nickel-aluminum bronze.<sup>42</sup>

wrought alloys for seawater service. Nickel-aluminum bronzes are used as castings. This means that, even if they suffer selective phase attack, bronze parts are generally so thick that the problem does not lead to catastrophic failure. All copper alloys are subject to dealloying in stagnant seawater, perhaps due to hydrogen sulfide ( $H_2S$ )-generating biofilms.

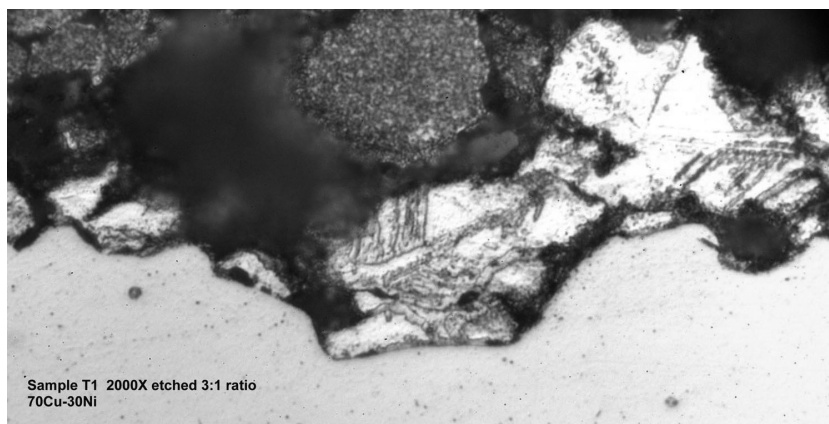
### EROSION CORROSION

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. This can be the result of fast fluid flow past a stationary object or it can result from the quick motion of an object in a stationary fluid, such as happens when a ship's propeller churns the ocean. Other terms include flow-enhanced or flow-accelerated corrosion, which also include mechanisms not related to erosion corrosion.<sup>4,45</sup> These other flow-enhanced corrosion subjects are discussed elsewhere in this book, for example, in the section on pipelines. In erosion corrosion mechanical effects predominate.<sup>46</sup> Wellhead components like the one shown in Figure 5.40 sometimes fail within weeks due to sand production or erosion from small liquid droplets from a gas stream.

Surfaces which have undergone erosion corrosion are generally fairly clean, unlike the surfaces from many other forms of corrosion.

### Mechanism

Erosion corrosion is often the result of the wearing away of a protective scale or coating on the metal surface. Many people assume that erosion corrosion is associated with turbulent flow. This is true, because all practical piping systems require turbulent flow. The



**Figure 5.39** Dealloying on 70-30 cupronickel condenser tube in stagnant seawater.<sup>44</sup>

fluid would not flow fast enough if lamellar (nonturbulent) flow were maintained.

Most, if not all, erosion corrosion is caused by multiphase fluid flow. The flow regime maps shown below in Figure 5.41 indicate the distribution of liquid (dark areas) and vapor (light areas) in vertical and horizontal flow. Slug flow has serious velocity-related problems, but none of these patterns produce erosion corrosion in straight piping in the absence of entrained solids. Where a flow pattern changes, for example, at a rough pipe connection, or a wellhead, liquid droplets or impinging

gas bubbles, which can collapse and produce shock waves that spall the protective surface film, or solid particles can cause accelerated attack by removing the protective film, either a passive film, mineral scale, or corrosion inhibitor film. These flow regime maps do not indicate the effects of entrained solids, for example, sand, corrosion products, or scale, all of which are known to accelerate erosion corrosion.

### Velocity Effects

**ANSI/API RP14E** Most metals have a critical velocity, which is the highest fluid velocity that can be tolerated before erosion corrosion will occur. For topside equipment piping, this is defined by a formula in ANSI/API RP 14E:<sup>47</sup>

$$V_{\max} = \frac{C \times A}{\rho^{0.5}} \quad (\text{Eq. 5.1})$$

where:

	SI	FPS
$V_{\max}$ = critical (maximum) velocity	m/s	ft/s
$\rho$ = density	kg/m <sup>3</sup>	lbm/ft <sup>3</sup>
A = conversion constant	1.23	1

The ANSI/API recommended values for the C-factor are:

- C = 100 for solids-free continuous service
- C = 125 for solids-free intermittent service
- C = 150–200 for solids-free, noncorrosive continuous service
- C = 250 for solids-free, noncorrosive intermittent service.



Figure 5.40 Eroded wellhead component.<sup>9</sup>

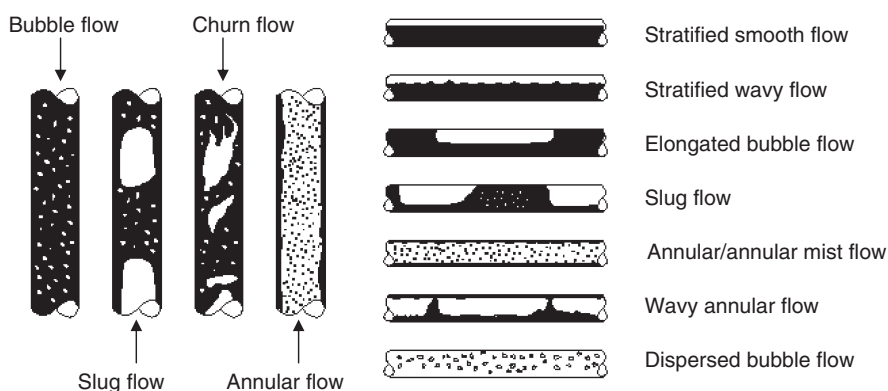


Figure 5.41 Multiphase fluid flow regimes in straight runs of vertical or horizontal piping.

Solids-containing lines should have significantly reduced maximum allowable velocities, although no specific guidelines are offered.

The same recommended practice suggests a minimum velocity in two-phase flow of approximately 10 ft/s (3 m/s) to minimize slugging in separation equipment. This is more important if elevation changes are involved.

The practice does not consider fluid properties such as viscosity, effects of solid particles, substrate materials properties such as hardness, and geometric properties such as elbows and flow constrictions. All of these properties are known to affect erosion-corrosion resistance.<sup>48</sup>

**Downhole Applications** While the ANSI/API recommended practice is written for topside service piping systems, it has also been used for downhole production tubing and for injection wells. If the recommended maximum velocities are too conservative, they can cause major losses of production. Setting the limits too high means erosion, possible equipment failure, and potential loss of production. Most companies consider the guidelines too conservative and operate with C-factors of 400 or greater and injection water (not multiphased fluid) velocities of up to 50 ft/s (15 m/s) for CRAs (e.g., 13Cr).<sup>49</sup>

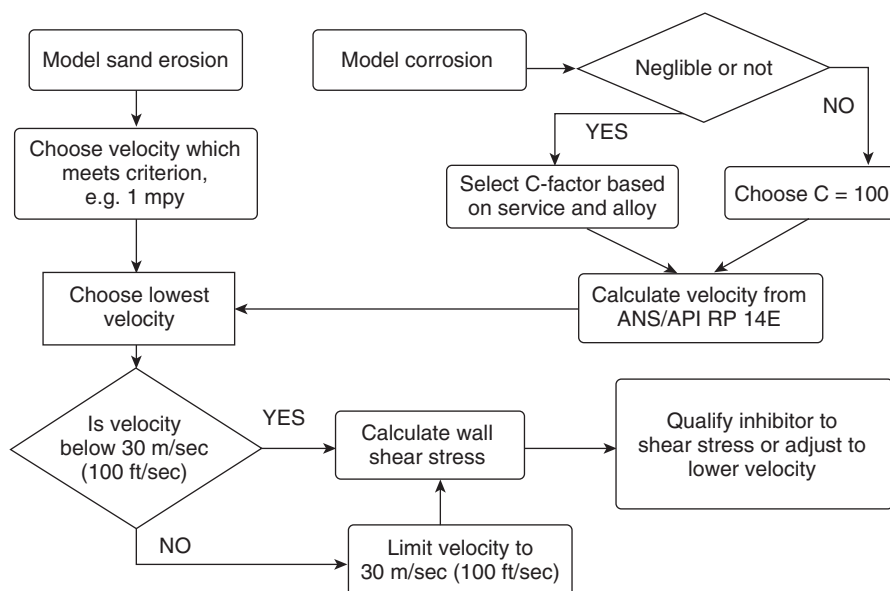
**Effects of Different Environments on Maximum Velocity** Some companies have developed proprietary in-house guidelines on how to calculate maximum allowable velocities. Variables included in some of

these guidelines are shown in Table 5.2. C-factors range from 200 for continuous use of carbon steel with no inhibitor in multiphase oil and gas wells (higher than the RP14E guidelines) to 450 for nickel-based alloys in all of the environments and other CRAs in dry gas injection. Other models are used for sand erosion, which is not considered in the RP 14E process. The total procedure is modeled in Figure 5.42.

The question of appropriate maximum velocities for downhole applications is a subject of continuing controversy and ongoing research. The subject is complicated, with over 30 parameters reported in the literature, and no consensus on this subject is likely.<sup>48–53</sup>

**TABLE 5.2 Erosion-Corrosion Variables for Choosing C-Factors in ANSI/API RP 14E**

Systems	Material Choice
Seawater	Carbon steel without inhibition
Single phase production (all liquids)	Carbon steel with inhibition
Multiphase production (oil wells or gas wells)	13Cr and Modified 13Cr
Dry gas injection (no corrosion, no liquids)	Duplex Stainless Steel
Methanol (no corrosion)	Super Duplex Stainless Steel Ni-Based CRAs



**Figure 5.42** Erosion-corrosion decision process for downhole tubing.

## Materials

Erosion corrosion of carbon steel is due to erosion of scale on the surface. Duplex and austenitic stainless steels have passive films that quickly reform, and these materials are erosion-corrosion resistant. Martensitic stainless steels, 13Cr alloys, are intermediate between the other two and show the effects of both erosion and corrosion.<sup>48</sup>

Most of the previous discussion has concerned topside piping and downhole OCTG applications, but other oilfield applications have erosion-corrosion problems as well. Condenser tubes have erosion problems at the tube inlets, and Table 5.3 shows recommended water velocity limits for condenser tubes in seawater.

## Cavitation

The erosion corrosion that has been discussed so far has been due to moving fluids or solids impacting against a stationary metal surface. Cavitation is somewhat different, because it usually causes damage due to rapid movement of a metal surface in such a manner that a liquid, for example, in a pump, undergoes a rapid loss of pressure which causes the liquid to form vapor bubbles. This release of vapor bubbles is not harmful, but if the same bubbles collapse against a metal surface, as shown in Figure 5.43, damage of the surface film(s) results in fresh metal exposures which then corrode. Cavitating pump impellers and housings can undergo rapid attack. Designing pumping systems to avoid the occurrence of cavitation, normally by maintaining a positive head on the liquid, is one means of avoiding this problem.<sup>54</sup> Another is to use hard-facing alloys on pump components. Figure 5.44 shows a pump impeller that was damaged due to cavitation. Note how the damage is on the downstream (low-pressure side of the impeller

vanes). This 316 stainless steel (UNS S31600) was in service for 1 year.

## Areas of Concern

Erosion corrosion is a possibility whenever changes in fluid flow patterns occur, especially when they are

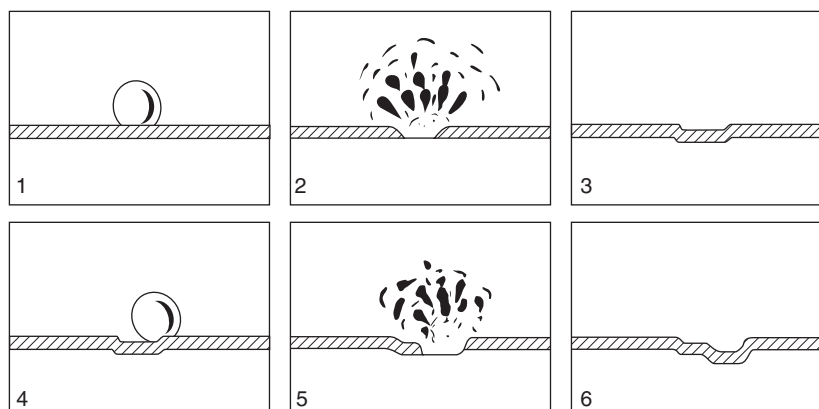
**TABLE 5.3 Suggested Velocity Limits for Condenser Tube Alloys in Seawater**

Alloy	Design Velocity That Should Not Be Exceeded	
	(ft/s)	(m/s)
Copper	3 <sup>a</sup>	0.9 <sup>a</sup>
Silicon bronze	3 <sup>a</sup>	0.9 <sup>a</sup>
Admiralty brass	5 <sup>a</sup>	1.5 <sup>a</sup>
Aluminum brass	8 <sup>a</sup>	2.4 <sup>a</sup>
90-10 copper nickel	10 <sup>a</sup>	3.0 <sup>a</sup>
70-30 copper nickel	12 <sup>a</sup>	3.7 <sup>a</sup>
Ni-Cu alloy 400	No maximum velocity limit <sup>b</sup>	
Type 316 stainless steel	No maximum velocity limit <sup>b</sup>	
Ni-Cr-Fe-Mo alloys 825 and 20Cb3	No maximum velocity limit <sup>b</sup>	
Ni-Cr-Mo alloys 625 and C-276	No velocity limits	
Titanium	No velocity limits	

<sup>a</sup> In deaerated brines encountered in the heat recovery heat exchangers in desalination plants the critical velocities can be increased from 1 to 2 ft/s (0.3 to 0.6 m/s).

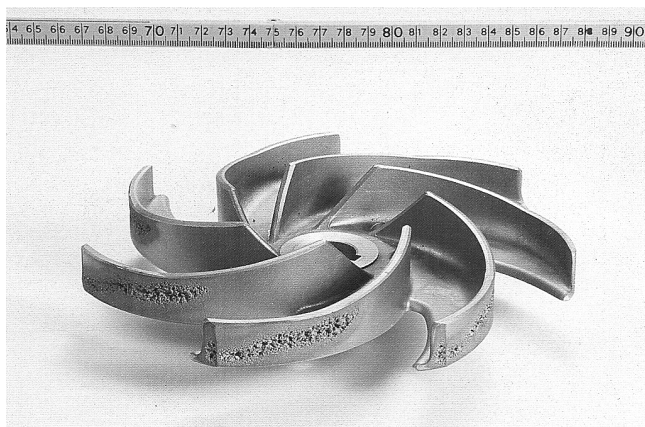
<sup>b</sup> Minimum velocity 5 ft/s (1.5 m/s).

Source: F. L. LaQue<sup>24</sup>, *Marine Corrosion: Causes and Prevention*, p. 267, John Wiley and Sons, 1975. Reproduced with permission of the Electrochemical Society.



**Figure 5.43** Cavitation bubble collapse and subsequent corrosion. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.





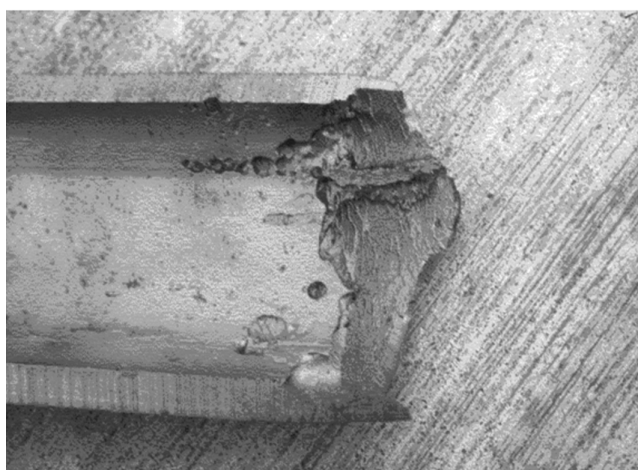
**Figure 5.44** Erosion corrosion due to cavitation on a stainless steel pump impeller.<sup>55</sup>

accompanied by concurrent changes in pressure or temperature. This can be downstream of flow restrictions, where additional turbulence and phase changes have been introduced, as well as at locations of local flow disruption.

**Wellheads** Erosion corrosion is normally handled in wellhead and Christmas tree equipment by making the equipment from erosion-resistant materials. The additional thickness of the castings common in wellhead equipment allows for some metal loss. It is common to use hard-facing liners on carbon steel components in these locations. This reduces the cost compared to making the entire assembly of an erosion-corrosion-resistant alloy.<sup>12</sup>

**Pumps** Erosion corrosion in pumps is treated in a number of ways. Like wellhead equipment, many pump components are made from castings and are fairly thick. This provides erosion tolerances that are sometimes sufficient, provided that inspection during downtimes is possible. The cavitation damage shown in Figure 5.44 can be minimized by placing pumps in locations where sufficient positive head is available to prevent cavitation. Damage to large pumps is often repaired using hard-facing alloys, typically nickel-cobalt alloys, that are applied by welding or flame-spray processes. The use of erosion-resistant alloys is also important. Many large seawater pumps made from bronzes, for example, nickel-aluminum bronzes, may have erosion-corrosion problems caused by improper foundry techniques that produce unwanted phases in the alloy that then undergo selective phase attack (a form of dealloying), leaving soft surfaces that can then be eroded.

**Downhole Tubing** Downhole tubing can have erosion-corrosion problems caused by localized turbulence near



**Figure 5.45** Eroded downhole tubing from an offshore production platform.

joints. This is shown in Figure 5.45, which shows erosion corrosion of downhole tubing from an offshore production platform in the North Sea. This platform received major attention when downhole erosion was reported shortly after production started.<sup>56,57</sup> Downhole multiphase fluid flow regimes are seldom as simple as shown in Figure 5.41. Deviations from vertical flow can often exceed 45 degrees and can sometimes approach horizontal flow. This means that inspection tools must check in the most likely locations for damage, and asymmetrical damage of downhole tubing has been reported.<sup>56</sup>

Note how most of the tubing surfaces shown in Figure 5.45 are not corroded. This is due to a combination of protective iron carbonate scales from the production fluid and the action of corrosion inhibitors where the scales have been breached. In situations where the scale is eroded, as shown in Figure 5.45, the corrosion inhibitor dosages may be inadequate to cover the exposed



**Figure 5.46** Erosion corrosion of an elbow in natural gas piping.

metal surfaces, and the fluid velocities may be too fast and erode the inhibitor films from the exposed metal.<sup>58</sup>

**Condenser Inlets** Condenser inlets are another area of erosion-corrosion concern. The first few centimeters of condenser tubes are prone to erosion corrosion, and a common method of minimizing this problem is to use plastic inserts that expand upon wetting and line the tube near the inlet. The loss of heat transfer is minimal, because the thermally insulating polymers extend only a short distance into tubing that is usually several meters long. This is more of a problem with soft condenser tube materials, for example, cupronickel and other copper alloys. The trend to the use of titanium for seawater piping offshore has minimized this problem because titanium is much more erosion resistant.

**Erosion in Elbows and Bends in Piping** Figure 5.46 shows erosion corrosion of carbon steel piping near an elbow in a natural gas pipeline. The additional turbulence at sharp bends in piping causes accelerated erosion, especially when solids are entrained in the system. Liquid droplets can also impinge at piping bends and produce similar erosion patterns. This is shown in Figure 5.47. Notice the localized erosion damage. It is very important to inspect in the proper locations to monitor if erosion is occurring. Placing an ultrasonic probe only a few centimeters away from the damage would miss it entirely. This problem has caused many utility systems to develop erosion modeling software to allow plant inspectors to determine where their



**Figure 5.47** Erosion corrosion in a carbon steel steam pipe.<sup>55</sup> Photo courtesy of NACE International, reproduced with permission.

periodic inspections should occur. The miles of piping in a typical power plant are too extensive to allow 100% inspection.

Steam injection systems in oilfield operations are even more complicated than power plant piping, and software for predicting where inspections should occur is not available. Any potential inspections are complicated, because most erosion-subject steam injection piping is covered with insulation, and the quality of steam (presence or absence of water droplets) is likely to be lower in injection systems.

One potential remedy to minimize erosion corrosion in steam piping is to increase the radius of any bends in the piping. This, of course, means increased installation costs, and space limitations, especially offshore, will often prevent this approach.

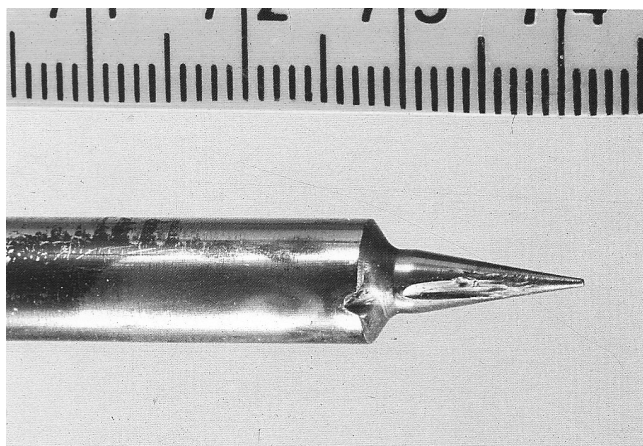
**Seals and Control Surfaces** Seals are locations where erosion corrosion can be very rapid. Improperly placed seals, or the relative motion of components at sealed joints, can create small openings that can be rapidly eroded, often within hours, once high-pressure steam or other fluids start leaking. This is shown in Figures 5.48 and 5.49. In both cases, the eroded material was a relatively soft austenitic stainless steel, and the use of a harder erosion-resistant material (e.g., chrome-cobalt alloys) was appropriate.

**Additional Areas of Concern** It has been estimated that up to 15% of failures in oil and gas production are due to erosion corrosion in gravel packs, nozzles, and Christmas trees before they reach a first separator.<sup>59</sup> The equipment features most likely to experience erosion corrosion are shown in Table 5.4. Erosion corrosion is most likely to happen with particulates, for example, sand production, although liquid droplets and cavitation can also produce problems.





**Figure 5.48** Erosion corrosion of a stainless steel seal in a steam line. Time to failure was hours.



**Figure 5.49** Erosion corrosion through a pin (spindle) in a pressure-reducing valve for a high-pressure boiler. Time to failure was a few days.<sup>55</sup> Photo courtesy of NACE International, reproduced with permission.

**TABLE 5.4 Equipment Features Susceptible to Erosion Corrosion<sup>60</sup>**

Chokes	Most vulnerable
Sudden constrictions	
Partially closed valves	
Standard radius elbows	
Weld intrusions	
Pipe bore mismatches at flanges	
Reducers	
Long radius elbows and mitre elbows	
Blind tees	
Straight pipes	Least vulnerable

## Control

Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion-resistant alloy. Alterations in fluid velocity and changes in flow patterns can also reduce the effects of erosion corrosion. Chemical treatment with corrosion inhibitors may require much higher dosage levels than are required in the absence of erosion corrosion. This is because erosion removal of protective films may expose much higher bare metal surface areas. If solid particle erosion is involved, most corrosion inhibitors will adhere (chemisorb) to the particles as well as to bare metal.

Prediction of erosion corrosion locations and severity is limited, and there is no clear consensus on how to determine erosion thresholds. For this reason, monitoring in likely erosion locations once production has started is the primary means of controlling the effects of erosion corrosion.<sup>61</sup>

## ENVIRONMENTALLY INDUCED CRACKING

Environmental cracking is often defined as the brittle failure of an otherwise ductile material due to the presence of tensile stresses and a specific environment. The stresses involved in environmental cracking can be from applied loads or from residual stresses caused by manufacturing and construction processes. The overall macroscopic stresses associated with this cracking are generally much below the yield stresses of the alloys in question. This cracking can result in the sudden rupture of structures, especially pressure vessels such as pipelines, and this sudden failure can lead to significant safety concerns.

Because of safety concerns and the widespread occurrence of environmental cracking in many industries and environments, it is the form of corrosion most studied in research laboratories worldwide. Unfortunately, despite decades of research, no consensus on the mechanism(s) of environmental cracking is available, and the classification of environmental cracking remains controversial.

At one time, stress corrosion cracking (SCC) was considered an anodic phenomenon, and hydrogen embrittlement (HE), due to cathodic hydrogen charging, was considered to be another form of environmental cracking.<sup>4,33</sup> This idea is controversial, and no clear consensus on the mechanism is likely. While the mechanisms of some forms of environmental cracking remain unclear, approaches to minimize the problem are available and will be emphasized in this discussion. In the absence of a consensus on this subject, this discussion

**TABLE 5.5 Metals and Environmental Cracking Environments<sup>46</sup>**

Metal	Environment	Factors That Increase Risk of SCC
Carbon steels	Hydrogen sulphide	Increasing H <sub>2</sub> S, moderate temperatures, more acidic, higher strength/hardness, higher stress levels
Carbon steels	Carbonates	Higher strength
Carbon steels	Chlorides	Higher strength, higher stress levels, more acidic
Copper alloys	Ammonia	Higher strength, higher stress levels
Martensitic stainless steels	Hydrogen sulphide	Increasing H <sub>2</sub> S, moderate temperatures, more acidic, higher strength/hardness, higher stress levels
Austenitic stainless steels	Chlorides	Higher strength, higher chloride levels, higher stress levels, more acidic, higher temperatures, presence of H <sub>2</sub> S
Duplex stainless steels	Chlorides	Higher strength, higher chloride levels, higher stress levels, more acidic, higher temperatures, presence of H <sub>2</sub> S
Titanium	Alcohol	Higher stress levels, lower water content

will treat environmental cracking in accordance with the guidance available in NACE/ISO RP010156, the most widely used oilfield standards on the subject.<sup>33,62,63</sup> There are a wide variety of terms used to describe environmental cracking, including SCC, season cracking, corrosion fatigue, HE, caustic embrittlement, and liquid metal embrittlement. Many oilfield personnel will use the term SCC as a synonym for all of the above terms.

One clear consensus is that most environmental cracking, with the exception of corrosion fatigue, occurs due to a combination of tensile stresses and specific corrosive environments. Corrosion fatigue can occur in any corrosive environment. A few oilfield environments are listed in Table 5.5. It is apparent from Table 5.5 that H<sub>2</sub>S and chlorides are common to environmental cracking in most oilfield environments. Despite all of the research on environmental cracking, no screening tests have been developed that identify new environments, and all of the alloy–environment combinations have been identified due to field failures.

At one time, environmental cracking was considered to be a problem of certain alloys in certain environments. Unfortunately, every structural alloy system has some environment where cracking is known to occur.<sup>64</sup> Note that in the following discussion, there are some mechanisms where the stresses come from chemical reactions either on the surface or within the metal. This concept of environmental cracking is a major departure from the idea of tensile stresses (applied or residual) found in the general (as opposed to oilfield) literature.

## SCC

This term is used for most aqueous environmental cracking that is not clearly associated with hydrogen or H<sub>2</sub>S. The most common characteristic of environments

that cause this form of corrosion is the presence of chlorides, although copper-based alloys stress corrode in ammonia and other nitrogen-containing environments. Many environments that cause SCC are only mildly corrosive insofar as other forms of corrosion are concerned. It is not unusual to see SCC on surfaces that otherwise seem to be uncorroded, or only mildly corroded, at least to the unaided eye.

SCC initiation sites include pits, metallurgical defects, surface discontinuities, intergranular corrosion, and other stress raisers.<sup>65</sup> SCC is often unaccompanied by visible corrosion products and may appear to be the result of strictly mechanical causes. This is shown in Figures 5.50–5.54. Note the “river branching pattern” of cracks in Figure 5.55. This branched-crack appearance is direct evidence of SCC, and no other metallurgical failure mode produces this pattern of cracking. The absence of this branching should not be taken as evidence of a lack of SCC, because many metals, to include high-strength steels, may reach a critical flaw size and fail by SCC before the crack has extended long enough to start branching. Cracks as short as a fraction of an inch (several millimeters) have been known to produce SCC failures in high-strength steel and other materials.

The growth of stress corrosion cracks is discontinuous and is thought to usually involve initiation and first-stage propagation, secondary steady-state propagation, and final rapid failure. HE has been proposed as the mechanism whereby these stages occur, although this is disputed by some researchers. The strongest evidence for hydrogen-related mechanisms is in high-strength ferritic steels.<sup>65</sup> In the presence of active corrosion, usually pitting or crevice corrosion, the cracking is generally called SCC, but many authorities suggest that this should more properly be called hydrogen-assisted stress corrosion cracking (HSCC). This form of corrosion





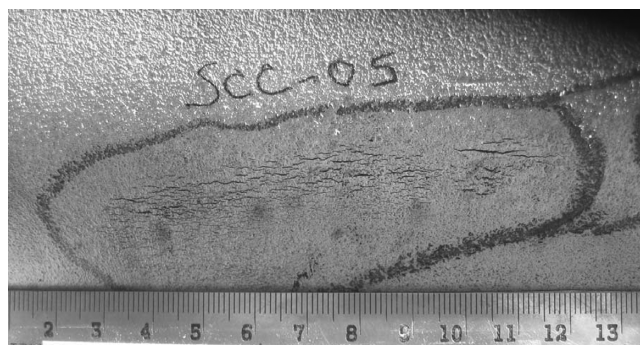
**Figure 5.50** Stress corrosion cracking underneath insulation on a stainless steel condensate line. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.



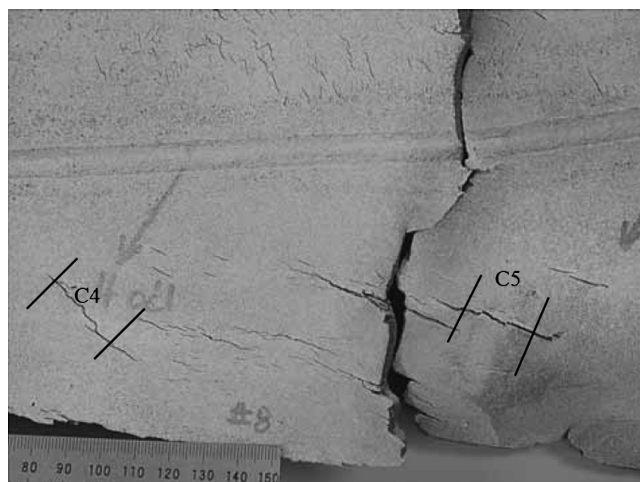
**Figure 5.51** Multiple branching cracks typical of many stress corrosion cracking failures.<sup>55</sup>

cracking can occur in almost any acidic environment where hydrogen reduction is the cathodic reaction. Increasing the strength and hardness levels of carbon steel, high-strength low-alloy steels, and martensitic stainless steels often increases susceptibility to this form of cracking.<sup>67</sup>

Carbon steels and other ferritic steels are the most commonly used metals in oilfield environments, and the



**Figure 5.52** Clustered "colonies" of stress corrosion cracks on the outside of a carbon steel pipeline.<sup>66</sup>

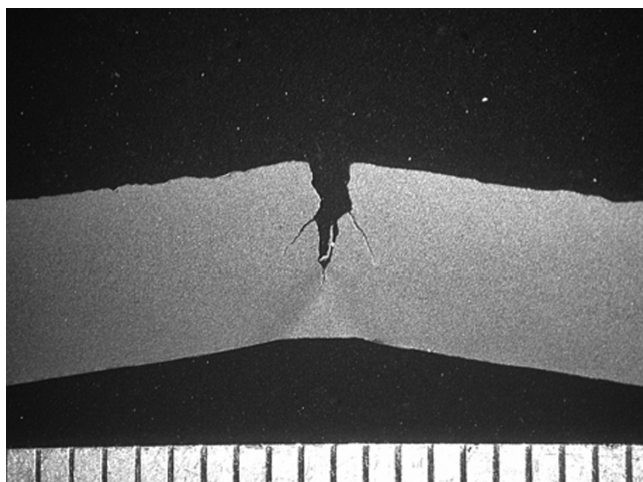


**Figure 5.53** Small cracks joining together and intersecting circumferential cracks on the exterior of a pipeline.<sup>68</sup>

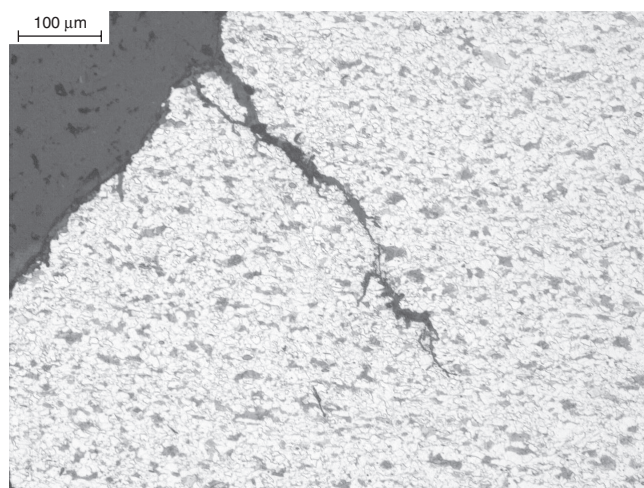
possibility of hydrogen involvement in the SCC mechanism(s) is an indication that corrosion control methods based on cathodic protection must be used with caution. This is one reason why pipelines, where corrosion control is normally by a combination of protective coatings and cathodic protection, are seldom constructed out of high-strength (yield stresses greater than 80ksi [550MPa]) steel. Most cathodic reduction reactions on carbon steel pipelines are due to oxygen reduction, but the possibility of hydrogen reduction, especially beneath disbonded protective coatings, is a potentially serious concern.

Unlike the controversy associated with mechanisms of SCC in steels, there is no dispute that SCC in titanium alloys can involve hydrogen, and hydrides of titanium have been detected in titanium after SCC events.

Stress corrosion cracks often appear in groups or colonies on otherwise uncorroded surfaces. This is shown in Figure 5.52, which shows intersecting cracks on the outside of a buried pipeline during external exca-



**Figure 5.54** Typical cross section of secondary cracks showing mid-wall bifurcation.<sup>68</sup>



Mag. Approx.  $\times 150$

**Figure 5.55** Transgranular SCC in pipeline steel.<sup>68</sup>

vation and examination. Cracks, either internal or external, will often grow together until they reach a critical flaw size that may lead to final rupture. This is shown in Figure 5.53, where small cracks have joined together and a circumferential crack has grown around a pipeline.

Cracks often branch as they progress into the metal. There are a number of reasons for this branching, which is shown in Figure 5.54 for the same pipeline that is shown in Figure 5.53. Note how the crack splits at approximately the mid-wall location in the pipeline and how the outside surface is generally roughened, even though only one crack seems to have started at the surface shown in this picture.

SCC can progress in an intergranular (between the crystals) or a transgranular (across the crystals) manner. This is one means that failure analysts have used to

determine the causes of cracking, for example, in pipeline steels where the pH of the surface moisture may influence whether cracking is intergranular or transgranular.<sup>68</sup> Figure 5.55 shows the transgranular nature of cracks in the pipeline steel shown in Figures 5.53 and 5.54. While this analysis has proven useful in analyzing the causes of SCC in buried pipelines, many cracks will change mode during the crack progression.<sup>4</sup>

SCC is controlled by avoiding metal-environment combinations that cause this problem. Additional methods of SCC control include various methods of stress relief, for example, post-weld heat treatment, protective coatings, corrosion inhibitors, and cathodic protection. Much of this control, for example, in pipelines, is devoted to avoiding the formation of stress risers, small defects on metal surfaces that serve as initiation sites for SCC which, once started, may be difficult to control.

**Caustic Embrittlement** Caustic embrittlement is one of the first forms of environmental cracking or SCC to receive widespread industrial attention. Boiler water is treated to a pH known to reduce corrosion rates (typically about pH = 8–9) by treatment with sodium hydroxide. If water evaporation produces higher pH fluids, for example, in crevices or at points where tubes meet restraints such as headers or baffles, the pH can increase to levels as high as 14, and this can cause intergranular cracking of carbon steels. Caustic cracking is controlled by the use of buffers, which prevent the buildup of high pHs, and by the substitution of ammonium hydroxide for sodium hydroxide. At high temperatures the ammonia evaporates, which deprives the hydroxide ( $\text{OH}^-$ ) ions of the necessary cation to balance electrical charge and prevents the buildup of excessive pHs.<sup>69</sup> The principals of boiler water treatment were developed in the 1920s by the U.S. Bureau of Mines, and recent advances have come from a variety of companies that specialize in boiler water treatment chemicals. Most oil-field operators rely on guidance from these specialized water treatment suppliers.

### HE and $\text{H}_2\text{S}$ -Related Cracking

The small size of hydrogen atoms means that hydrogen can readily dissolve in most metals. The dissolution of hydrogen into metals comes from two common sources: the reduction of hydrogen ions at cathodes in electrochemical cells due to corrosion or electroplating and the entry of hydrogen into metals from environments having hydrogen-entry promoters such as  $\text{H}_2\text{S}$  and cyanides. These environments produce small amounts of monatomic hydrogen which usually combine to form molecular (diatomic) hydrogen molecules, which are too large

to dissolve into metals. In the short time that monatomic hydrogen atoms exist on surfaces, small amounts of monatomic (nascent) hydrogen dissolve into the metal substrate and follow diffusion paths from locations of high concentrations (the source surface) to regions of lower concentration (the metal interior and usually the opposite surface). This dissolution is usually at interstitial sites (between the atomic locations of the metal). Several forms of hydrogen degradation are associated with the recombination of internal hydrogen atoms to form hydrogen molecules, which are too large for interstitial diffusion through the metal lattice. Other forms of HE are due to mechanisms that are not presently understood and are the subject of research controversies.

HE and other hydrogen-related problems can occur in any  $H_2S$ -containing environment and in electroplated metals even in the absence of environmental hydrogen. Another source of monatomic hydrogen is welding, and improper welding procedures can introduce monatomic hydrogen into metals.

There are a wide variety of hydrogen and  $H_2S$ -related cracking phenomena encountered in upstream environments. Many of the classifications discussed below follow terminology in NACE MR0175/ISO 15156, which emphasizes the choice of materials for use in  $H_2S$  environments.<sup>33,62,65</sup>

**HE** Small quantities of hydrogen inside certain metals make them susceptible to subcritical crack growth under stress. Metals can also have major decreases yield strength and undergo brittle failures in hydrogen-containing environments. Both processes are commonly called HE. Oilfield metals with HE problems include high-strength steels, aluminum, and titanium, although most problems occur in high-strength steels. The exact mechanisms of HE in steels have not been established, and no iron hydrides have ever been reported, but brittle intermetallic hydrides have been found in titanium and other hydrogen-embrittled metals. Ferritic steels, for example, carbon steels and low-alloy steels, are considered to be more susceptible than austenitic alloys.

The initial 1975 version of NACE RP0175 limited  $H_2S$  exposures to metals having a hardness of HRC22 or less which, depending on the size and shape of the metal, correlates to yield strengths of approximately 80 ksi (550 MPa).

The sudden propagation of brittle fractures may be time delayed and occur months, even years, after exposure to hydrogen. This is a characteristic failure mode in plated metal components. It is thermodynamically impossible to electroplate metals such as zinc or chromium onto steel without also generating hydrogen gas,

some of which invariably dissolves into the steel. The standard way of compensating for this inevitable introduction of hydrogen into the metal substrate is to use an elevated-temperature bake-out procedure of several hours, depending on metal thickness, at temperatures around 175–205°C (350–400°F).

Higher-strength steels are considered to be more susceptible than lower-strength alloys, and work hardening seems to be preferable to heat treatment, for example, in high-strength cables.<sup>2</sup> Concerns for HE are the reasons that very high-strength wire, used in downhole wireline applications, must be allowed to outgas for days between downhole trips. Many authorities consider the highly cold-worked metals used in these wires to be less susceptible to hydrogen effects than thicker metals, usually heat-treated for strength, at the same strength (or hardness) levels. The presence of multiple defects, primarily dislocations, is thought to serve to minimize the accumulation of hydrogen in any one location and to minimize formation of subsurface molecular (diatomic) hydrogen considered to be associated with HE.

Hydrogen charging, the introduction of monatomic hydrogen into metals, can come from the breakdown of water at elevated temperatures in welding processes. This is the reason for protective, water-impermeable coatings on most welding rod.<sup>70</sup>

Charging can also occur on cathodes at defects exposing steel underneath anodic protective coatings, for example, zinc-plating. This is the reason that galvanizing (zinc coatings) is not allowed on high-strength fasteners.<sup>71</sup>

HE is considered to be a relatively low-temperature phenomenon, and most failures seem to occur at temperatures below 100°C (212°F). Prolonged exposure to high temperatures can have counteracting effects. More hydrogen may be generated on metal surfaces due to accelerated corrosion or other chemical reactions, but atomic diffusion and subsequent outgassing is also enhanced.

**Hydrogen Stress Cracking (HSC)** This is a term used in NACE RP0176/ISO 15156 to describe cracking in a metal due to the presence of hydrogen in a metal along with residual or applied tensile stresses.<sup>62</sup>

It is used to describe cracking in metals that are not sensitive to sulfide stress cracking (SSC) but which are embrittled when galvanically coupled as cathodes to corroding anodes. The term galvanically induced HSC is applied to this mechanism of cracking. The discussion above on HE of galvanized bolts would be considered to involve HSC by many oilfield authorities, although this is not the terminology used outside the oilfield industry.



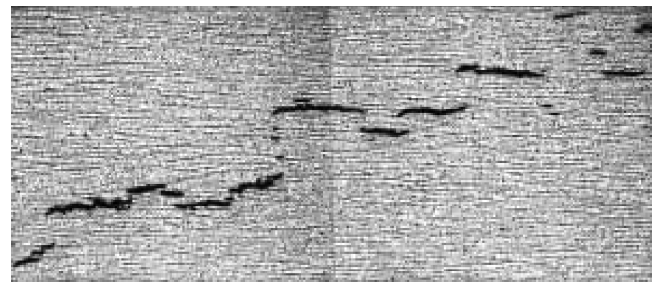
**Hydrogen-Induced Cracking (HIC)** HIC, also known as stepwise cracking, in carbon and low-alloy steels is caused by atomic hydrogen diffusing into the steel and forming hydrogen molecules internally at trap sites, such as vacancies in the metal, grain boundaries, dislocations, and second-phase particle boundaries, to include inclusions.<sup>70–73</sup> HIC is a form of hydrogen-related cracking that does not require tensile stresses, either applied or residual, to produce cracking. This lack of applied stresses is the main differentiation between HIC and SCC. HIC is a major concern in the  $H_2S$  environments covered by NACE SP0176/ISO 15156 and in other environments, for example, strong mineral acids ( $H_2S$  is a weak mineral acid), known to produce HE.<sup>62</sup>

Figure 5.56 shows HIC in pipeline steel.<sup>74</sup> Note how the cracks form parallel to the rolling direction of the steel and how they tend to be planar—relatively long and flat. Modern pipeline steels are treated with calcium that reduces the total volume of inclusions and tends to form hard, rounded inclusions which should present fewer locations for HIC to form.<sup>75</sup>

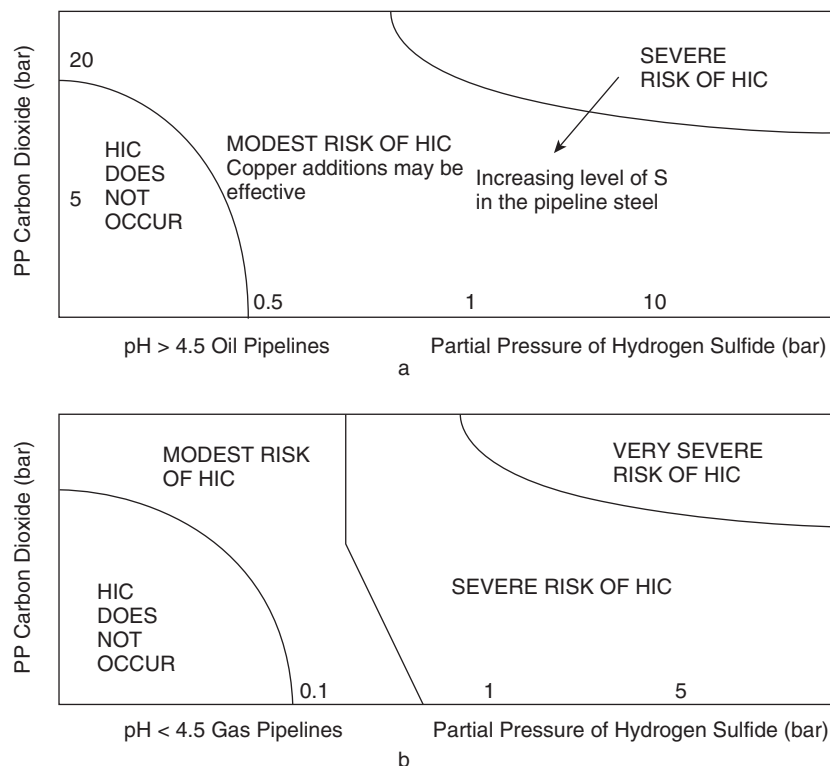
Figure 5.57 shows environmental conditions where HIC is considered important for pipeline steels. The combinations of carbon dioxide ( $CO_2$ ) and  $H_2S$  in the environment shown in this figure are approximate, but

they are used for determining environments where HIC-resistant steels are necessary. Many operators assume that virtually all oil fields will eventually sour and require  $H_2S$ -resistant materials, but some gas fields are depleted so quickly that this may not be necessary.

HIC susceptibility has been shown to be greatest in high-sulfur steels and to be less likely in modern, low-sulfur steels. However, in low-sulfur steels other considerations, such as the presence of ferrite-pearlite banding, also promote HIC. Condensate waters in gas systems lack the mineral buffering available from formation waters that accompany crude oil. For this reason, gas



**Figure 5.56** Hydrogen-induced cracking (HIC) in pipeline steel.<sup>74</sup>





systems are likely to have acidic environments and are usually more corrosive than crude oil systems. If the gas contains  $H_2S$ , then the gas systems will require  $H_2S$ -resistant materials of construction.<sup>76</sup>

**SSC** This common form of environmental cracking (SSC) is considered to be a form of HIC. It requires a residual or applied tensile stress and the combined presence of water and  $H_2S$ , which indicates that some organizations would consider this to be a form of SCC, although this is not the interpretation in NACE RP0175/ISO 15156.<sup>62</sup>

Susceptible alloys, especially steels, react with  $H_2S$ , forming metallic sulfides and monatomic nascent hydrogen. This monatomic hydrogen forms as a reduction reaction product and diffuses into the metal matrix, causing internal cracking. High nickel contents, which limit surface corrosion and also cause the microstructure to have austenite, a more resistant phase than the ferrite common in carbon and low-alloy steels, greatly improve the resistance to SSC. SSC is worst around  $80^\circ C \pm 20^\circ C$  ( $176^\circ F \pm 36^\circ F$ ). Above this temperature, hydrogen is more mobile and is likely to diffuse from the metal before forming internal defects leading to cracking. The term SSC is applied to cracking in liquid water environments.

#### ***Stress-Oriented Hydrogen-Induced Cracking (SOHIC)***

Applying stresses to steel with HIC can result in interconnecting cracks between the hydrogen-induced cracks. The result is relatively long cracks in the through-thickness direction of a structure, for example, a pipeline.<sup>62</sup> This is shown in Figure 5.58, where the small hydrogen-induced cracks have been joined by connecting cracks, resulting in considerably less resistance to applied stresses. The linking of hydrogen-induced cracks is referred to as SOHIC or as stepwise cracking.

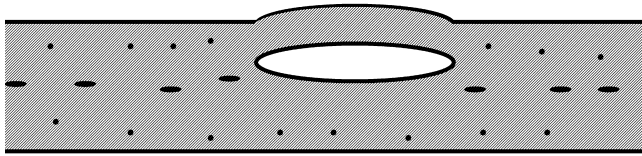
Susceptibility to SOHIC can be complicated, as low-sulfur modern steels, thought to be resistant to this form of damage, have been found to have additional problems associated with the metallurgical treatments of newer steels used in repair and new construction. The HIC shown in Figure 5.56 could lead to SOHIC in the presence of applied stresses, for example, the hoop stresses found in pressurized pipelines.

**Hydrogen Blistering** The small cracks discussed above in sections on HIC, SSC, and SOHIC are sometimes referred to as small blisters. Another use of the term hydrogen blistering is for hydrogen gas blisters that form inside structures that become so large that their deformations can be seen macroscopically as surface deformations. These larger blisters form in the same

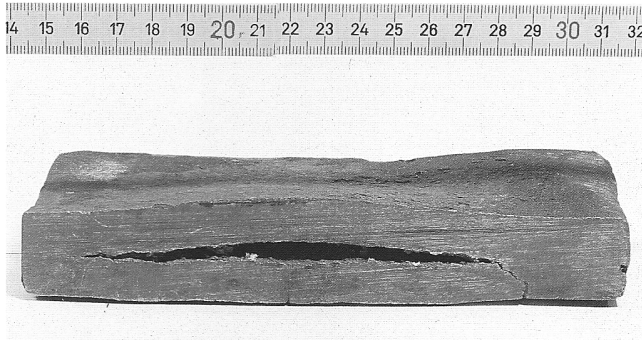


**Figure 5.58** Stress-oriented hydrogen-induced cracking (SOHIC).<sup>73</sup>

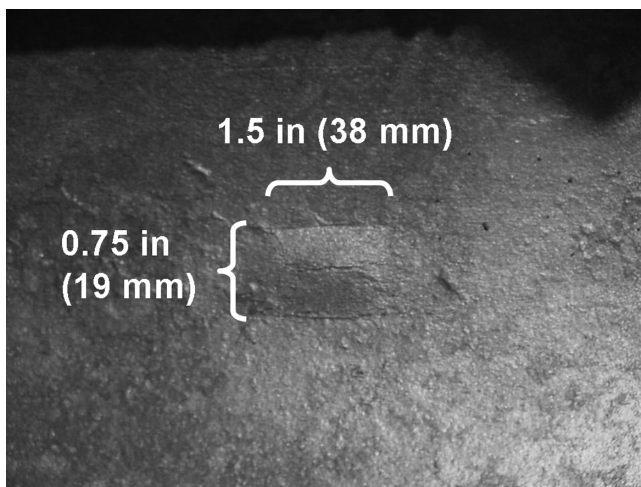
way as the smaller cracks. Hydrogen diffuses into the steel and then gets trapped at locations where migration is hindered, and the recombination of thermodynamically unstable monatomic hydrogen to thermodynamically stable diatomic hydrogen molecules is most likely to happen. The most likely sites for this to happen are near large ceramic inclusions (impurities) within the steel. Figure 5.59 shows schematically how these inclusions are likely to be arranged in steel plate and other thick sections. As a result of the hot rolling process, ceramic inclusions near plate surfaces are more likely to be broken up and become smaller. Near the center of plate steel there has been less plastic deformation, and both the steel crystals and the inclusion particles tend to be larger. As hydrogen migrates through the steel, the chances for monatomic atoms to meet and become trapped are greater near the larger inclusions near the center of the plate. This is the reason why plate steel, especially the relatively low-quality, inexpensive plate steel used for storage tanks and similar structures, is more likely to produce hydrogen blistering. Many of these blisters form near the center of plate steel and can



**Figure 5.59** Schematic representation of ceramic inclusions (dark marks) and hydrogen blister formation in plate steel.



**Figure 5.60** Hydrogen blister formed on wall plate of a CO<sub>2</sub> scrubbing tower.<sup>55</sup>



**Figure 5.61** Hydrogen blister on the inside of a crude oil pipeline.

become several inches (centimeters) in horizontal dimension.

Common locations for hydrogen blisters include the bottoms of above-ground storage tanks, where acidic waters can concentrate, and the walls of tanks and process equipment. Figure 5.60 shows blisters in the wall of a CO<sub>2</sub> scrubber, and Figure 5.61 shows blisters in a crude oil pipeline that collected sour crude for many years.

The quality of steel determines the resistance to hydrogen cracks and blisters of all types. Pressure vessel

steels are not immune to this problem, but it is much less common in the highly processed and refined low-alloy steels used for most process pressure vessels.

Typical treatments for hydrogen blistering depend on the application. For storage tank bottoms, which are loaded in compression, it is fairly common to locate the boundaries of the blisters with ultrasonic inspection. Then, at a predetermined distance from the boundaries, a plate is welded over the blister, and the blister is left in place. Other organizations carefully pierce the blister using non-sparking drills to relieve the pressure before welding a patch over the surface. Similar procedures are sometimes used on tank walls, and monitoring the growth of blisters has been reported.<sup>55</sup>

In pressure vessels, it is common to grind the blisters out of the metal. This grinding to a predetermined distance beyond the detected limits of the blister is intended to remove both the overlying “blister” steel, which serves no structural purpose, and also to eliminate any microcracking that has not been detected by the inspection process. The remaining wall thickness is then determined. While welding repairs are sometimes performed to replace the missing metal, it is more common to determine the maximum allowable operating pressure of the equipment and to downgrade the service if necessary. If reductions in operating pressure are inadvisable, then external repairs (sleeves, clamps, etc.) are used to increase the effective wall thickness in the area of concern. The same downgrading or external reinforcement procedures are used for pipelines, but it is seldom feasible to grind out the blisters, especially if they are internal.

The best way to avoid hydrogen blistering is by the use of higher-quality, lower-inclusion steel, and this is the reason that most hydrogen blisters are encountered in above-ground storage tanks and other large structures where the economics of construction from higher-grade steel are not justified and inspection and repair of occasional blisters is an accepted alternative.

### Hydrogen Attack

High-temperature hydrogen environments can cause hydrogen to diffuse into the metal and react with the carbon in the iron carbides (cementite) in steel. The resulting formation of gaseous methane can cause blistering similar to HIC or hydrogen blistering. This form of attack, while a concern in refining, is seldom a concern in upstream operations.

### Liquid Metal Embrittlement (LME)

Liquid metals can attack solid metals and produce fractures similar to those found in other forms of

environmental attack. Both intergranular and transgranular attack is known to occur. This form of attack can happen during welding and other processes, but careful removal of low-melting coatings, for example, zinc coatings, prior to welding normally solves this problem.

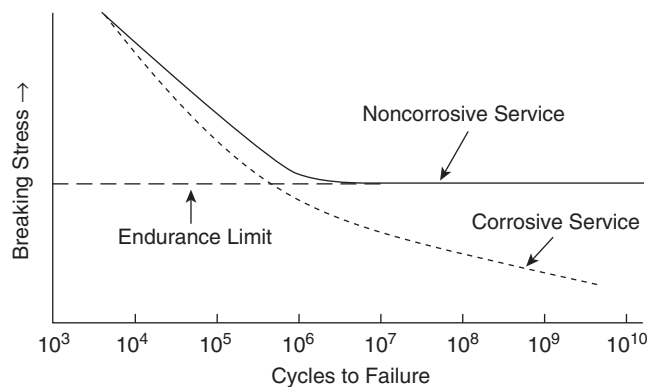
Most concerns with LME in upstream operations are offshore and relate to safety in fires and to cracking of brazed aluminum heat exchangers, which are used in cooling natural gas to reduce the volume before injecting it into a pipeline for transmission to shore.

Many operators have banned the use of aluminum or galvanizing for offshore platform structures, for example, hand rails and ladders, because of a concern that these liquid metals could cause embrittlement of carbon steels and stainless steel if the lower-melting zinc or aluminum were to melt in a fire. The counter argument to this thinking is that by the time temperatures have reached the melting point of these metals, it is too late for the equipment concerned. No firm guidelines on this question exist, and many operators are now using aluminum, for example, for decks, ladders, handrails, and helidecks. The thin layers of zinc on galvanized structures are not considered adequate corrosion protection for most offshore structural members. Galvanizing is commonly used for corrosion resistance in bolts and similar fasteners, often with an overlay of an organic coating for ease of disconnect. In some locations, cadmium, which is banned for toxicity reasons by some authorities, is the preferred anodic coating material for fasteners, although it is seldom applied to larger components.

Brazed aluminum heat exchangers are used for offshore cooling of natural gas, because of their weight savings over other metals. To avoid cracking by liquid mercury, which is eventually found in virtually all natural gas formations, it is standard practice to place mercury removal processes in the gas treatment stream prior to the brazed aluminum heat exchangers used for cryogenic cooling.<sup>76</sup>

### Corrosion Fatigue

Corrosive environments lower the fatigue life of many oilfield components and structures. This is shown schematically in Figure 5.62, which shows the elimination of the fatigue or endurance limit due to the presence of a corrosive environment. It is possible to cyclically stress a component so quickly that the effects of corrosion are minimal, and it is also possible to introduce components so corrosive that they corrode to failure before the effects of cyclic stresses become significant. It is very hard to predict the cumulative effects of corrosion and fatigue. The simplistic ideas shown in Figures 4.16 and



**Figure 5.62** The reduction in fatigue resistance due to a corrosive environment.

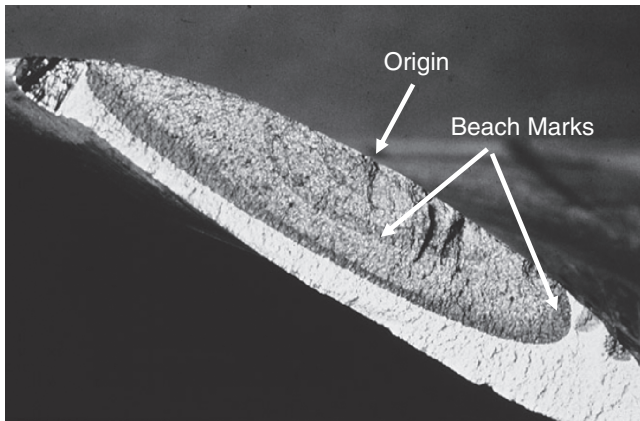
5.62 assume that the cyclic stresses are the same on each repetition. This is approximately true for many rotating shafts, sucker rods, and so on, but it is far from true for wave loading on offshore structures and for many other oilfield applications.

Fatigue cracks, like many other forms of environmental cracks, often start at stress raisers such as corrosion pits, machined notches, or surface scratches. Once corrosion starts, localized corrosion fatigue cracks develop occluded cell concentration differences compared to the external environment, and the interaction between chemistry and mechanical loading becomes very complicated and virtually impossible to predict or model. It thus becomes important to monitor likely fatigue sites for crack initiation and propagation in attempts to detect damage and correct the situation before fracture occurs.

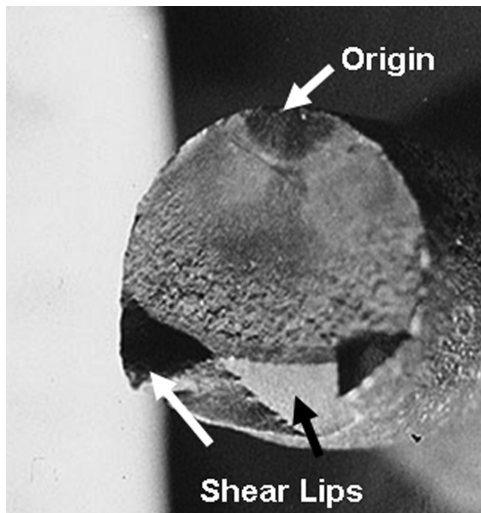
Figure 5.63 shows a typical corrosion fatigue fracture surface. The origin of the fracture surface is at the upper center of the picture and the crack grew radially from this origin, leaving indications of the crack progression, called beach marks or clamshell markings, which are indications that the equipment tarnished to different levels, possibly due to intermittent operation of the equipment or changes in the cyclic loading level. Once the crack reached a critical flaw size, the part broke, leaving a shiny fracture surface at the bottom of the picture. It is apparent that other surface defects started additional cracks in the lower right of this picture. The appearance of beach marks is a characteristic feature of many corrosion fatigue failures. Note how the fatigue fracture spread over most of the metal surface before the final tensile overload indicated by the shiny surfaces at the bottom of the picture.

Another corrosion fatigue fracture surface is shown in Figure 5.64. This oilfield sucker rod has a clearly defined origin, and beach marks indicate how the fracture spread from this origin due to cyclic loading. After





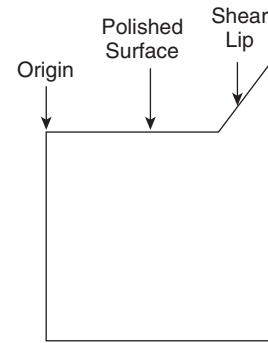
**Figure 5.63** Beach marks on the surface of a corrosion-fatigue surface from a marine propeller.



**Figure 5.64** Corrosion fatigue and shear lip formation on a sucker rod fracture surface. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.

the crack progressed across approximately one-half of the rod, the surface became rough, due to the fact that the crack remained open during compression strokes and did not polish the surface as much as near the origin. Once the crack reached a critical flaw size, the rod broke, forming shear lips at approximately  $45^\circ$  to the fracture surface. The shadows formed by the shear lips on the lower left and right of the picture appear as dark triangles in Figure 5.64. The bottom center of the picture shows where the metal pulled apart by shear, but the shear lip is down and away from the viewer. Most overload failures, to include fatigue failures, will form shear lips on the final fracture surface. A side view of this phenomenon is shown in Figure 5.65.

Most fatigue failures progress for significant distances before final overload failures, and inspection to



**Figure 5.65** Schematic showing the side view of a typical corrosion fatigue rod failure.

detect and monitor fatigue cracking is an important part of corrosion fatigue control. Methods of preventing corrosion, such as the use of more corrosion-resistant alloys, corrosion inhibitors, and cathodic protection are also helpful.

## OTHER FORMS OF CORROSION IMPORTANT TO OILFIELD OPERATIONS

There is no universally accepted terminology for corrosion, and the oil and gas industry has adopted a number of terms for corrosion that frequently overlap with the terms discussed in previous sections of this chapter. This section discusses some forms of corrosion commonly discussed in the oilfield literature and some other forms of corrosion likely to be encountered in oil and gas production.

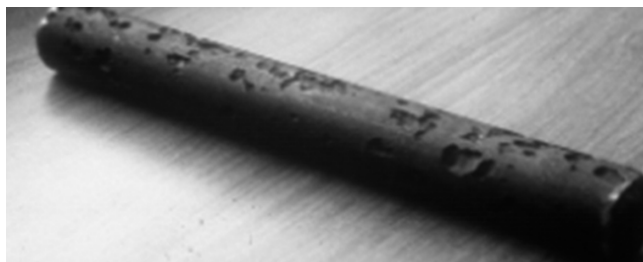
### Oxygen Attack

Oxygen attack normally refers to pitting corrosion due to the presence of dissolved oxygen in production fluids. This seldom occurs in downhole environments, and when it does, it is usually due to inadequate treatment of injection waters that were exposed to oxygen-containing air in topside processing and storage. The most common treatments for oxygen attack are mechanical deaeration treatment of the water plus the use of oxygen scavengers.

### Sweet Corrosion

This term, which is becoming outdated, refers to corrosion in environments where the corrosion is due to the presence of dissolved  $\text{CO}_2$ . Most production fluid corrosion, especially in natural gas production, is due to  $\text{CO}_2$ . The most common treatments for sweet or  $\text{CO}_2$  corrosion is the use of corrosion inhibitors. These





**Figure 5.66** Mesa corrosion of a 9-chrome sucker rod.

inhibitors become ineffective as the downhole temperatures and pressures increase.<sup>73</sup>

### Sour Corrosion

The term sour corrosion refers to corrosion that occurs in production fluids due to the presence of  $H_2S$ .  $H_2S$  is a weak mineral acid, and most corrosion reactions are relatively minor in these environments.

Figure 3.3 compares the effects of oxygen,  $CO_2$ , and  $H_2S$  on corrosion. It is obvious that  $H_2S$  is the least corrosive of the three gases. Most problems with  $H_2S$  are associated with hydrogen-related cracking and, while the environments associated with  $H_2S$  cracking are considered to be “sour,” the cracking is seldom referred to as sour corrosion.

### Mesa Corrosion

Mesa corrosion refers to corrosion in  $CO_2$  environments that produce relatively flat surfaces where the metal is protected by carbonate films, usually siderite ( $FeCO_3$ ). This corrosion is characterized as fairly deep pits in the form of sharp-edged holes that are considered to look like the flat-topped “mesa” (table topped) mountains found in the southwestern United States.<sup>5,77</sup> Mesa corrosion is shown in Figures 5.66–5.68. All three pictures show relatively flat surfaces with localized pitting where the partially protective carbonate films break down. Most control of  $CO_2$  (sweet) corrosion is by the use of corrosion inhibitors.

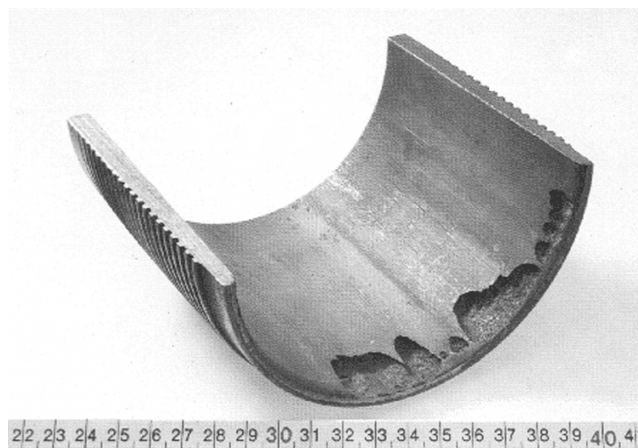
### Top-of-the-Line (TOL) Corrosion

The increased use of multiphase offshore pipelines and gathering lines has led to interest in top-of-the-line corrosion. This form of corrosion is shown schematically in Figure 5.69. Condensate, containing water high in  $CO_2$  and possibly acetic acid or other organic acids, aggressively attacks the top of horizontal pipelines where no corrosion inhibitor is present.

This condensation happens as the pipeline cools with distance from the compressor station. While corrosion



**Figure 5.67** Mesa corrosion on carbon steel plate.<sup>55</sup>



**Figure 5.68** Mesa corrosion at a threaded connection on downhole tubing.<sup>55</sup>

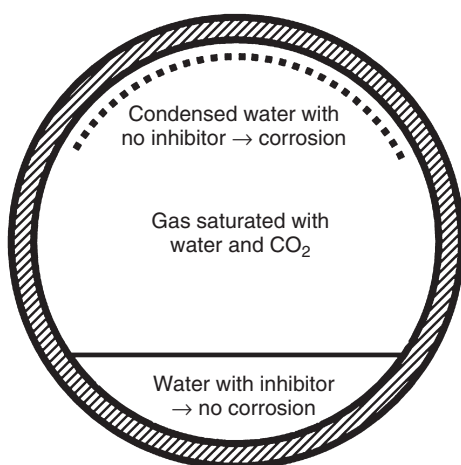
inhibitor can be maintained in the water phase at the bottom of the line, it is difficult to apply this inhibitor to the top of the line. Much effort concentrates on developments in modeling of where TOL corrosion is likely to occur and how delivery of corrosion inhibitors can be maintained. Research efforts include modeling the temperature profiles of subsea pipelines. This is shown in Figure 5.70, which shows the water dropout profile for a subsea pipeline.

Efforts to apply corrosion inhibitor to the inside top of multiphase pipelines include periodic pigging with

slugs of corrosion inhibitor.<sup>55</sup> TOL corrosion is an area of continuing research. Additional modeling includes pH profiles and other parameters that affect pipeline corrosion.<sup>78-84</sup>

### Wire Line Corrosion

Downhole inspection devices are often suspended using high-strength wires. These wires can cut into protective coatings and wear away corrosion inhibitor and protective scale films. An example of wire line corrosion is shown in Figure 5.71.



**Figure 5.69** Top-of-the-line corrosion in a multiphase pipeline.

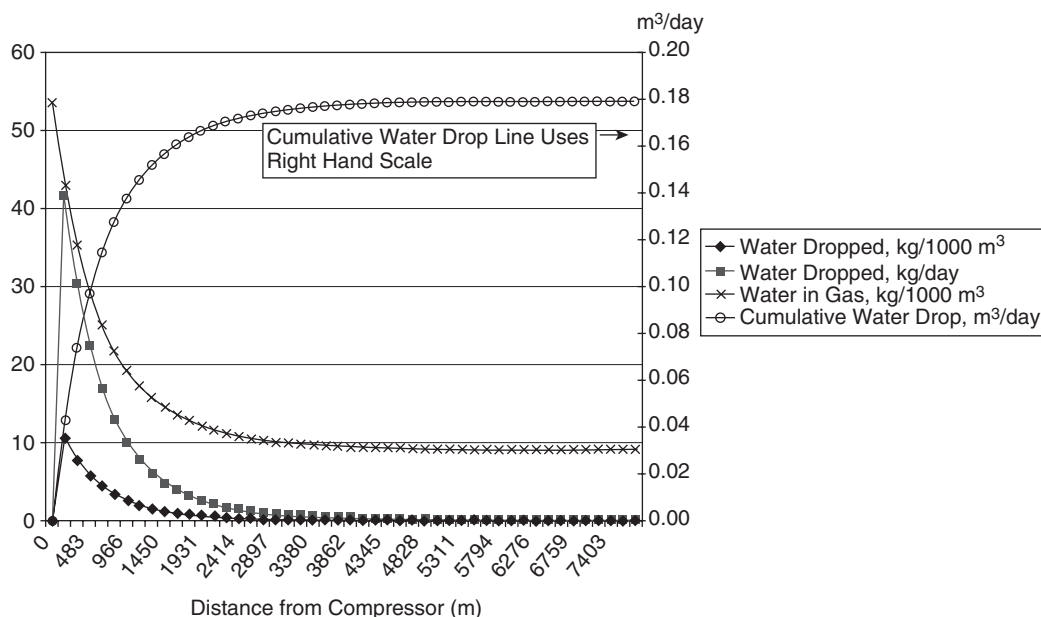
### Additional Forms of Corrosion Found in Oil and Gas Operations

The forms of corrosion discussed in this section are found in other industries, but they also occur in oilfield operations.

**Alkali Attack** Steam injection is a major means of secondary recovery in relatively viscous oil fields. Feedwater for steam production is normally treated to minimize the presence of minerals that would cause boiler deposits and limit heat transfer. If the boiler water treatment is inadequate or in deadlegs and crevices, the pH of the water can increase to such levels that significant corrosion can occur. This is shown in Figure 5.72. If mineral deposits due to precipitation of scale are not controlled, overheating of boiler tubes can occur, leading to tube swelling (creep) and rupture. These problems can be avoided by appropriate boiler feedwater treatment.

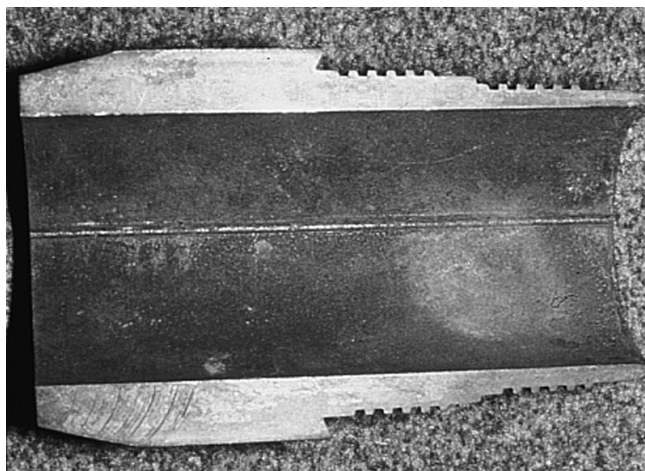
**Acid (Hydrogen) Grooving** Highly concentrated oxidizing mineral acids such as sulfuric acid are stored in carbon steel tanks. The concentrated acid forms a semi-protective film, and general uniform corrosion is normally acceptable for most sulfuric acid service. The gradual thinning should be monitored so that replacements can be planned at appropriate intervals.

Hydrogen grooving results when condensate, which is acidic but more corrosive than the highly concentrated liquid being stored, drips from locations where it

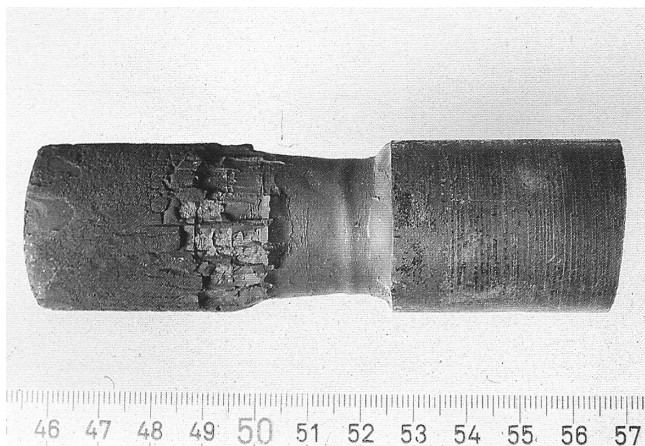


**Figure 5.70** Water dropout versus distance from pipeline compressor.<sup>77</sup>





**Figure 5.71** Wire line corrosion.<sup>9</sup>

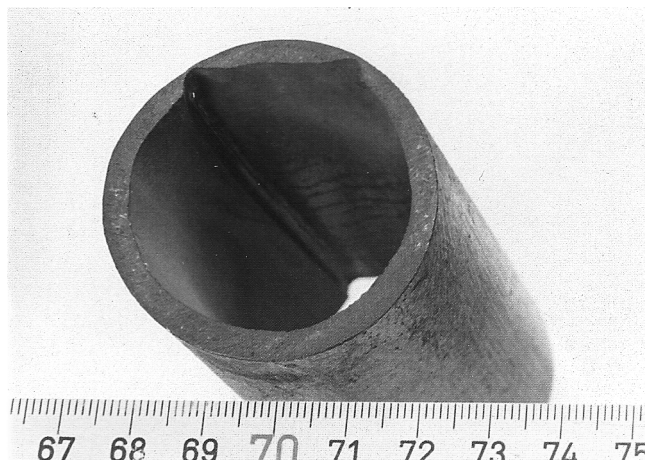


**Figure 5.72** Alkali attack at crevice in boiler water system.<sup>55</sup>

forms. This is typically the top of lines and below locations where acid is added to the tanks or piping systems. The corrosive condensate dissolves the passive film and creates grooves as shown in Figure 5.73.

The standard advice for control of hydrogen grooving is to use thick-walled piping, avoid stagnant situations where hydrogen gas bubbles can evolve in the same location over long periods of time and erode the passive film, and inspection of likely locations where wall thinning is likely.<sup>55,85</sup> Alloys, generally high-nickel alloys, are used for piping systems where the effects of fluid motion or of dilution, which makes the acid more ionic and therefore more corrosive, must be used in this type of service.

**CO<sub>2</sub> Channeling** Figure 5.2 shows general corrosion at the bottom of a gas well flowline. The relatively clean surfaces on the bottom of CO<sub>2</sub>-containing waterlines are characteristic of this form of corrosion. It is impor-



**Figure 5.73** Hydrogen grooving in sulfuric acid piping system.<sup>55</sup>

tant to limit the ingress of oxygen into CO<sub>2</sub>-containing flowlines of any type. CO<sub>2</sub> is a weak acid and is only slightly corrosive, but the combination of CO<sub>2</sub> plus oxygen produces a low-pH environment (due to the CO<sub>2</sub>) with relatively high concentrations of air (oxygen) that causes accelerated corrosion.<sup>55</sup>

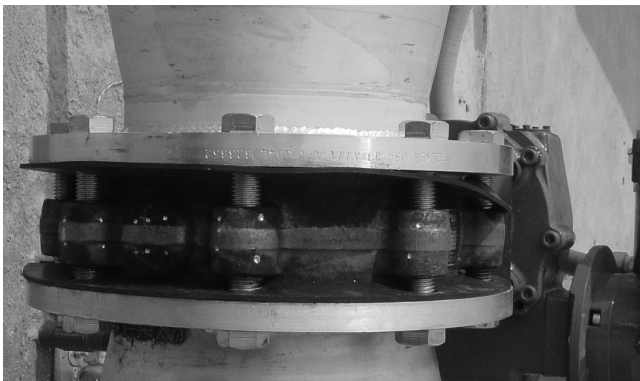
**Contact Corrosion** Contact corrosion is the result of small particles of suitable materials embedded in stainless steel. Carbon steel is a very common contaminant. It often comes from grinding operations that leave small particles of carbon steel, which are hard, embedded in the relatively soft stainless steel. The carbon steel particles form galvanic cells and quickly corrode, leaving pits on the surface which can then promote corrosion of the stainless steel.

Figures 5.74 and 5.75 show contact corrosion. The thin 316 stainless piping in Figure 5.74 corroded in a warm humid atmosphere after only 3 years. Eventual failure of the system would result without remedial action, most likely replacement of the piping in question. The valve shown in Figure 5.75 was discovered during post-construction inspection. While the discoloration of the valve material is unsightly, the stainless steel casting is so thick that no degradation in performance is likely.

Contact corrosion can be prevented by carefully choosing grinding media that do not contain metallic iron, by shielding stainless steel from contamination from nearby grinding operations, by avoiding the storage of stainless steel equipment on carbon steel racks, or by dissolving the embedded particles in aggressive pickling acids and then repassivating the stainless steel with nitric acid. As stated above, contact corrosion is not an engineering concern on thick-walled castings



**Figure 5.74** Contact corrosion on stainless steel piping caused by grinding debris from nearby carbon steel.<sup>55</sup>



**Figure 5.75** Contact corrosion on stainless steel valve components.

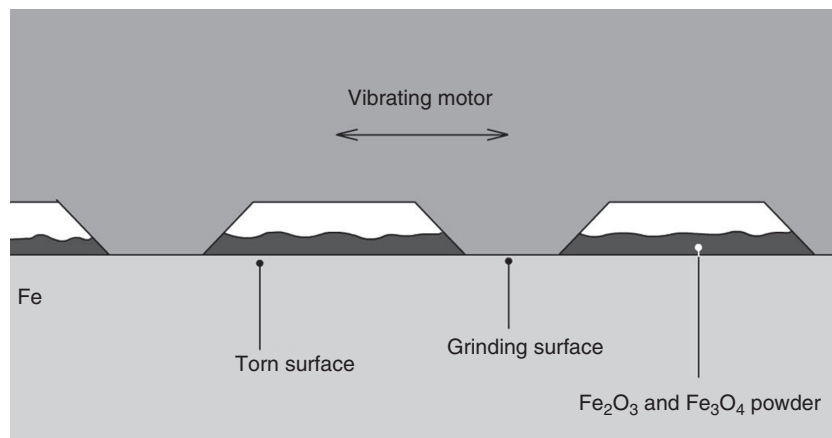
like the one shown in Figure 5.75, but it can lead to perforation in thinner components as shown in Figure 5.74.

It should be noted that some organizations, especially in Europe, use the term contact corrosion for galvanic corrosion, that is, galvanic contact corrosion.

**End Grain Attack** Figure 4.19 explained how the crystallographic structure is different in the three principal directions of plate metals. End grain attack has been shown in Figures 5.34 and 5.35, which show intergranular corrosion, and in Figure 5.68, which shows mesa corrosion. The point to remember is that the ends of crystals have closer spacing and are more likely to corrode than the flatter surfaces parallel to the rolling or forming direction.

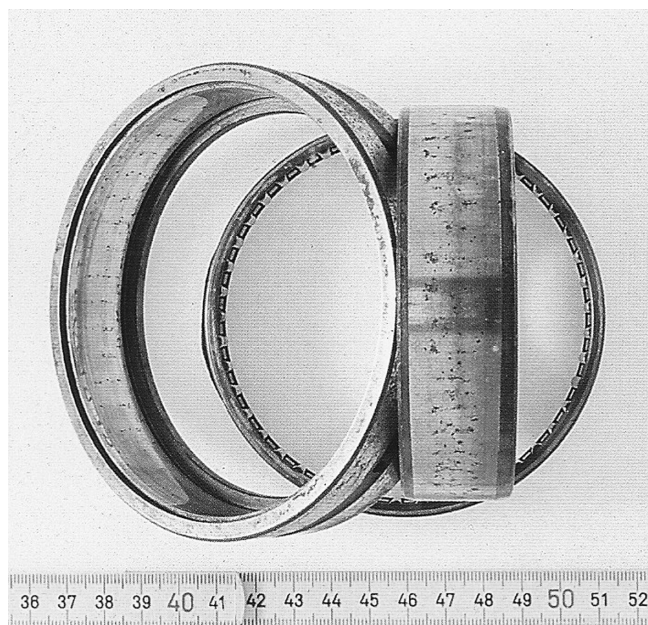
Many organizations use exposure samples of various types to monitor or measure corrosion rates. These small samples have different ratios of end grain versus parallel-to-forming direction crystal exposure, and this invariably produces different corrosion rates.

**Fretting Corrosion** Fretting corrosion happens when small oscillations in metal-to-metal contact abrade the protective films on metal surfaces and produce accelerated corrosion. It is similar to, and is often considered to be, a form of erosion corrosion. The concept of fretting corrosion is shown in Figure 5.76. This is a form of corrosion that is often found in standby equipment, where repetitive vibrations wear away protective films in the same location. This is shown in Figure 5.77 where a bearing race on a pump has suffered fretting corrosion. One means of limiting this form of corrosion is to operate the standby equipment for short periods at planned intervals, for example, weekly. The bearings are unlikely to stop in the same position after each



**Figure 5.76** Sketch illustrating the mechanism of fretting corrosion.<sup>13</sup>





**Figure 5.77** Fretting corrosion on roller bearing race.<sup>55</sup>

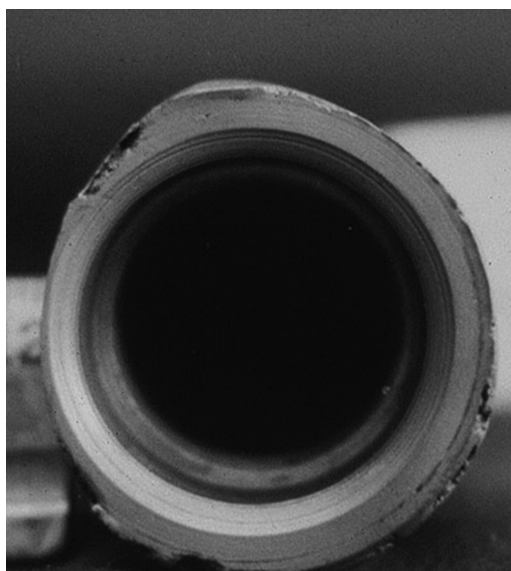


**Figure 5.78** Fretting corrosion of a shackle pin from an FPSO mooring chain. Photo courtesy of Ammonite Corrosion Engineering, <http://www.ammonite-corrosion.com/degrade.html>, accessed September 17, 2010.

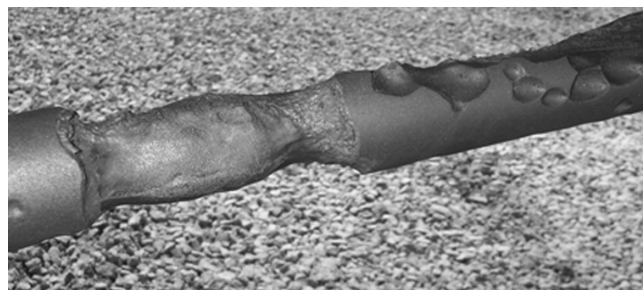
operation, and localized accelerated attack can be avoided.

Fretting corrosion can be found on many systems that are subject to vibrations. Figure 5.78 shows fretting corrosion from a shackle pin on a floating production, storage, and offloading (FPSO) mooring chain. Routine inspection for fretting corrosion should detect this form of corrosion before it leads to system failure.

Fretting corrosion is a major concern in heat exchangers, where vibrations cause damage at intermediate



**Figure 5.79** Uneven wear on downhole pump component. Photo courtesy of NACE Basic Corrosion Course, reproduced with permission.



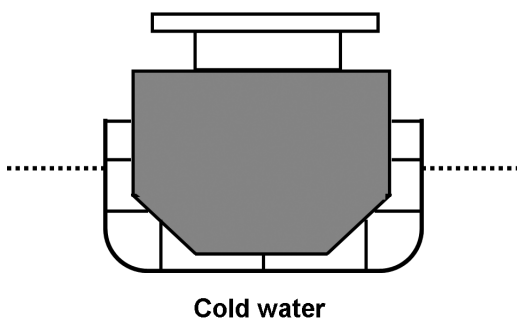
**Figure 5.80** Stray current corrosion of a stainless steel propeller shaft. Photo courtesy of Dudley Gibbs, Dudley's Marine Electric, Humacao, Puerto Rico, USA.

support baffles. Ultrasonic inspection is used to monitor wall loss at the baffle locations.

Downhole wear of moving parts, like the pump component shown in Figure 5.79, is more likely in deviated wells. Many offshore wells are more horizontal than vertical, and this can become an increasing problem.

**Stray Current Corrosion** Stray current corrosion can be caused by improperly grounded welding equipment, reversed polarity on impressed current cathodic protection systems, telluric currents, and a number of other sources. Many organizations rely on electrical isolation systems like those shown in Figures 5.9–5.11.

Stray current corrosion can produce any of the forms of corrosion discussed above, but it is more common to be diagnosed in situations where rapid widespread general corrosion, like that shown in Figure 5.80, occurs.



**Figure 5.81** Cross section drawing of double-hulled tanker showing annular space where condensation leads to accelerated “thermos bottle corrosion” for tankers carrying warm cargo in cold waters.

The stray current corrosion of the small boat propeller shaft shown in Figure 5.80 was caused by improper grounding of the electrical system on the boat in question.

Oilfield applications where stray current corrosion is likely to occur include pipelines sharing rights of way and other situations where impressed current cathodic protection causes stray current corrosion on nearby well casings.<sup>2,86–88</sup>

**Thermos Bottle Corrosion** The introduction of double-hulled tankers has created new corrosion concerns related to the operation of these tankers in cold water, where cold water on the exterior hull creates a “thermos bottle effect” and increased condensation leading to corrosion in the annular spaces between the external hull and the interior cargo tanks. This is shown schematically in Figure 5.81.

Many FPSO vessels are converted tankers. When operating in cold waters, the thermos bottle effect can be expected to lead to accelerated corrosion. Most corrosion control in the annular spaces on FPSO vessels is by protective coatings, and it is important that the annular spaces be designed so that inspection and maintenance can be accomplished. In addition to corrosion in these annular spaces, fatigue is an important concern in these vessels.<sup>89–94</sup>

## ADDITIONAL COMMENTS

The wall thickness for many applications is determined by calculating the wall thickness that meets mechanical requirements, such as pressure and weight of equipment, and adding an extra thickness called the corrosion allowance to account for the metal loss expected during the equipment design life. Penetration rates may vary, so, in the absence of design codes that specify another

**TABLE 5.6 Metal Failure Frequency for Various Forms of Corrosion<sup>95</sup>**

Forms of Corrosion Failure	Occurrence (%)	
General	31	0.65
Stress corrosion cracking	24	
Pitting	10	
Intergranular corrosion	6	
Erosion corrosion	7	
Weld corrosion	5	24%
Temperature (cold wall, high temperature, and hot wall)	4	
Corrosion fatigue	2	
Hydrogen (embrittlement, grooving, blistering, and attack)	2	
Crevices	2	11%
Galvanic	2	
Dealloying	1	
End grain attack	1	
Fretting	1	
Total	100	100%

Source: R. J. Landrum<sup>95</sup>, *Designing for Corrosion Control*, NACE, Houston, Texas, 1989, table 1.3, p. 25.

procedure, it is common assign a safety factor of 2; for example, the corrosion allowance is often twice the anticipated general corrosion penetration.<sup>55</sup> While this very conservative corrosion allowance is generally acceptable in relatively small chemical process plants, this allowance (twice the anticipated necessary wall thickness) would be prohibitively expensive for most oil and gas production applications, and corrosion allowances are generally much smaller for oil and gas production.

The problem with corrosion allowances is that most corrosion is localized, and localized corrosion rates, for example, pitting or stress corrosion, are many times deeper than the rates associated with general corrosion. Approximately 70% of corrosion in a typical process plant will be due to forms of corrosion not addressed by corrosion allowances. Table 5.6 shows the forms of corrosion reported by corrosion engineers from a major chemical company over a period of several years. The general trends probably relate to oil and gas production. The major differences are probably the increase in frequency of HE and other H<sub>2</sub>S-related forms of cracking. Most concerns of engineers and management are related to pitting and environmental cracking (termed stress corrosion cracking in Table 5.6).

General corrosion can be detected and repaired on a routine maintenance basis. Other forms of corrosion, for example, SCC or HE, can result in sudden equipment failure and shutdown. Inspection and compensation for these events is a major concern that must be

considered in design, inspection, and maintenance procedures.

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## CORROSION CONTROL

Most corrosion control in oil and gas production, as well as in other industries, is by the use of protective coatings, water treatment and corrosion inhibitors, and cathodic protection. These services are often provided by contractors that specialize in one or more of these corrosion control methods. It is important that employees of operating companies understand the principles involved in these corrosion control techniques, and many advances in these methods are developed by oil and gas companies in cooperation with specialty contractors.

Coatings and inhibitors have much proprietary technology which changes with time and, equally important, depends on the quality of local suppliers. Cathodic protection does not vary as much worldwide, and this is the reason why it is dealt with in greater detail.

This chapter is intended to cover the principles of the three corrosion control methods under discussion. Additional information relating to specific types of oilfield equipment is discussed in Chapter 8, Oilfield Equipment.

### PROTECTIVE COATINGS

Protective coatings are the most commonly used means of corrosion control. They are the standard means of controlling external corrosion on everything from offshore structures to pipelines and process vessels. Protective coatings may also be used on storage tank, pipeline, and storage vessel interiors. The reasons for their widespread use include the ease and low cost of

application. Most protective coatings are applied by liquid paint systems, but metallic coatings and wraps are also used. Ceramic coatings are used on some industries, but their brittle nature limits their use in oilfield applications.

Liquid coatings can be lacquers, varnishes, or paint. The first two are usually single-phase liquids, but paints, which are more complex, are generally used because of their greater protective qualities. Most paints are based on organic chemistry, but inorganic coatings, for example, inorganic zincs (IOZs), are also available and are widely used.

Linings are protective coatings that are applied in thicker films, usually 5 mm (0.2 in.) or more. They are usually applied as solid films and find use on the interiors of storage and ballast tanks, process vessels, and large-diameter piping. Their use is relatively limited in oilfield applications.

The associated costs of applying a protective coating system to an existing structure are typically:

• Surface preparation	50%+
• Permits and scaffolding	30–35%
• Materials	~10%
• Inspection and other costs	~10%

More expensive coating materials may have longer service lives, and this means that the total costs of protective coatings over the service life of a structure may be lower than if less expensive coatings were to be applied.

### Paint Components

The components of paint coatings are pigments, binders, volatile vehicles, and additives.

Pigments are usually inorganic minerals or metal particles. They provide opacity and color, but they also provide corrosion protection. Their low permeability to water and oxygen migration provides corrosion protection. Maximum protection is provided by paints with high volumes of pigment in the cured paint film. Primer coatings are sometimes named after their pigments, for example, zinc-rich primers.

Metallic zinc pigments can provide cathodic protection to steel substrates at coating holidays. Aluminum is less likely to provide this protection. Aluminum-pigmented paints have advantages over zinc at higher temperatures, for example, in flares and on the exteriors of hot piping and process vessels.

Binders are necessary to hold pigment particles together and to provide adhesion to the underlying substrate, either protected metal, in the case of primers, or underlying paint films. Paint coating types are often classified by the binder, for example, polyurethanes, epoxies, and vinyls.

The binder/pigment ratio is an important parameter in determining the effectiveness of a paint film. Too much binder produces high gloss but may produce chalking after environmental exposure. Too little binder means that the pigment will not be adequately wetted leading to paint film porosity and the loss of corrosion resistance. The best corrosion protection is obtained with paints that provide high pigment volumes but still insure adequate wetting of the pigments.

Volatile vehicles, either water or organic solvents or dispersants, dissolve or disperse the binder and allow the coating to spread. Modern coatings have lower volatile components due to environmental and health concerns with volatile organic compounds (VOCs).

Some paints cure by evaporation of the vehicle and others, for example, epoxies, cure by chemical reactions that form thermosetting polymer binders. The reaction-based coatings tend to have fewer volatile components.

Other constituents added to paints include plasticizers, which lower the brittleness of the cured film, and anti-skimming and anti-settling agents necessary to keep the paint usable after transport before final use.

### Coating Systems

It is common for coating systems to have several layers which are usually characterized as primers, intermediate or midcoats, and topcoats. It is important that all layers of a coating system be compatible so that interlayer adhesion and unwanted chemical reactions between the layers is avoided.

Primers, the first coating to be applied, provide adhesion of the paint film to the substrate. They also provide

most of the corrosion protection and, if necessary, are designed so that they can “key” or bond to the outer coats.

Intermediate or midcoats provide a barrier to water passage. They may also smooth out the surface prior to the application of the topcoat. They also serve as bonding interfaces allowing adhesion to both the primer and the topcoat.

Topcoats provide the desired color to the coating system. Unlike the lower coatings, which need to bind to subsequent coatings and are usually rough on a microscopic scale, most topcoats also provide a smooth surface which promotes water runoff.

### Corrosion Protection by Paint Films

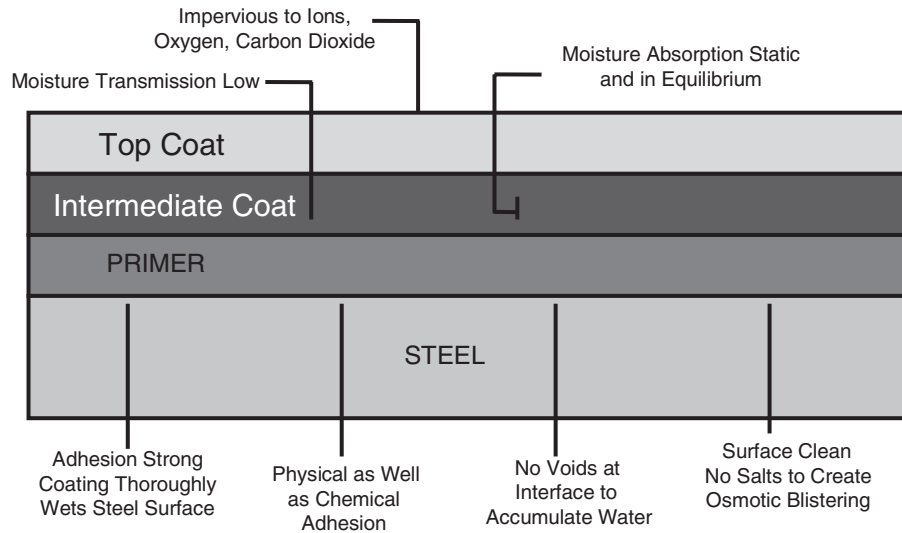
All paint films are permeable to moisture and oxygen to some extent, but their effect on lowering corrosion rates is due to the low permeability of the coatings compared with the uncoated environment.<sup>1-6</sup> The barrier concept is shown in Figure 6.1, which also shows the important properties of the primer, intermediate coat, and topcoat. Inorganic pigments in the primer provide most of the moisture and oxygen ingress barrier effect. Intermolecular spacings in polymers are much larger than in inorganic pigments, and most of the moisture permeates through the organic binders.

No coating system is perfect, and coating holidays, places where the coating is missing or has been removed, are locations where most corrosion occurs. One way of slowing corrosion at coating holidays is to have corrosion inhibitors in the pigment. This idea is shown in Figure 6.2. Several pigments that have been used for this purpose are listed below:

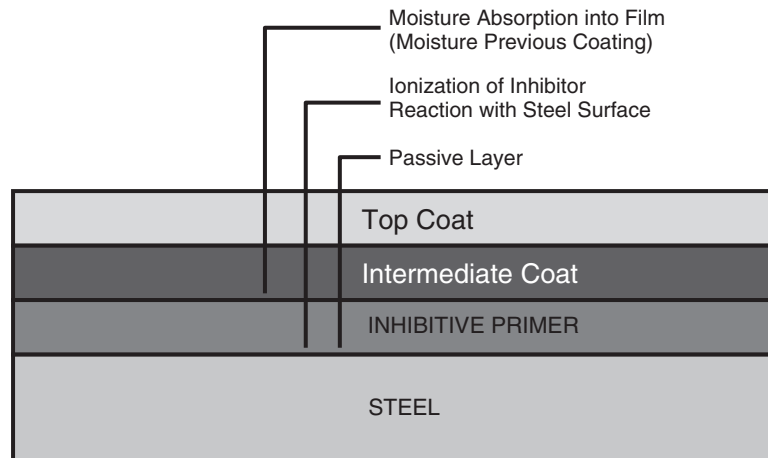
- Zinc chromate
- Zinc phosphate—the only pigment on this list not banned for environmental reasons
- Red lead
- Calcium plumbate (contains lead)
- Coal tar

Concerns with environmental damage have limited the use of corrosion inhibitors in pigments, and the use of chromates, the most effective of these pigments, has been largely replaced due to concerns with heavy metal pollution. Slow-release corrosion inhibitors are intended to release oxidizing agents which passivate the surface at holidays, but the nonavailability of chromates for this purpose has greatly reduced their effectiveness.

Metallic pigments, either zinc or aluminum flakes, are added as pigments to many primers. They are virtually



**Figure 6.1** Protective coating system serving as a moisture and oxygen permeation barrier. Drawing courtesy of NACE International, reproduced with permission.



**Figure 6.2** Protective coating system with slow-release corrosion inhibitors in the primer coat. Drawing courtesy of NACE International, reproduced with permission.

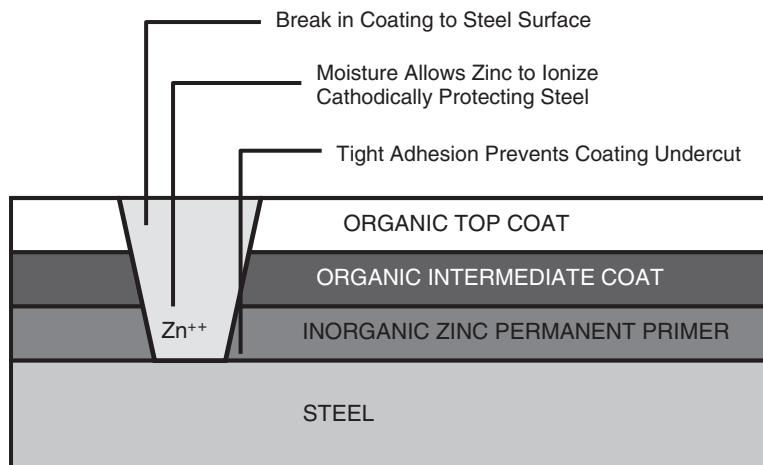
impermeable to moisture and oxygen migration. Zinc pigments also provide a measure of cathodic protection once the coating is breached. This cathodic protection is greatly reduced if the primer is overcoated, but this is often necessary for color coding or wear resistance reasons. IOZ primers are not subject to ultraviolet (UV) damage, so there is no need to overcoat them except for the reasons above. Organic zinc primers are also widely used, and they do benefit from overcoats.<sup>6</sup> Figure 6.3 illustrates the idea of using zinc-rich primers for cathodic protection at coating holidays.

### Desirable Properties of Protective Coating Systems

In addition to providing corrosion protection, coating systems should also have:

- Strong, durable bonding to the substrate
- Flexibility, because organic coatings have different coefficients of thermal expansion than metals, and coating flexure is inevitable
- Toughness, the ability to withstand mechanical shock and loading





**Figure 6.3** Inorganic zinc primer serving as the source of cathodic protection of the steel substrate at a coating holiday. Drawing courtesy of NACE International, reproduced with permission.

The choice of coating systems often requires compromises between these characteristics. As one example, very hard coatings such as are often used on pipeline exteriors are often difficult to repair if damaged in shipping and construction. The necessary bonding to undamaged coatings is hard to achieve. This problem is also apparent at field welds, where organic coatings must be removed prior to welding.

### Developments in Coatings Technology

Modern coating systems are generally longer lasting than those that were available in the past. Worker safety and environmental concerns have led to the development of new coatings having higher solids and lower VOC contents. The higher solids in modern coatings frequently lead to the need for better surface preparation, as many of these coating systems are less tolerant of surface contamination than the systems they are replacing. Electrostatic spraying is an application that was once confined to manufacturing of relatively small items, but recent developments allow for the use of electrostatic spraying in major new construction and rehabilitation. This technique is especially useful on complicated geometries where it is difficult to apply even coatings with other techniques.

### Useful Publications

The following publications provide guidance on coatings selection and on preparing contracts for protective coatings:<sup>7,8</sup>

- NORSOK M-CR-501, "Surface Preparation and Protective Coating"

- NACE Publication 6J162, "Guide to the Preparation of Contracts and Specifications for the Application of Protective Coatings"

The Norwegian standard is directed toward offshore platform construction, whereas the NACE standard also covers less harsh environments.

### Surface Preparation

Proper surface preparation is necessary for coatings to bond properly to metallic and other substrates. Most premature coatings failures can be attributed to improper surface preparation or to allowing the properly prepared surface to degrade before coatings are applied. Properly coated offshore platform deck coating systems sometimes last 30 years before recoating becomes necessary, but Figure 6.4 shows corrosion that resulted from poor surface preparation on an offshore platform deck after only 3 years. This failure could have been easily avoided.

The principal surface condition factors that are known to influence this performance are the presence of rust and mill scale, surface contaminants including salts, dust, oils and greases, and the surface profile, which must have enough roughness to allow mechanical adhesion between the primer and the bare metal surface but low enough so that paint covers the high spots with adequate cover.

Abrasive blasting is usually the preferred means of surface preparation, but high-pressure water jetting is becoming more common due to environmental and waste disposal concerns. Abrasive blasting leaves a rough anchor pattern on the metal surface, while water jetting usually does not. This has limited water jetting to



**Figure 6.4** Poor surface preparation led to a lack of coating adhesion and corrosion on this offshore platform deck in only 3 years.

cleaning metal surfaces for recoating, but modern developments with high-pressure water jetting are overcoming this lack of anchor pattern, and it is likely that the use of water jetting will supplant abrasive blasting for many projects in the future. Abrasive blasting to provide an anchor pattern is sometimes used on bare metal surfaces after they have been cleaned by water jetting. This blasting also removes any “flash rusting” that may have formed on the wet metal surface.

Neither of these techniques can remove grease and other organic contaminants from the surface, and solvents or other cleaning agents must be used prior to either blasting or water jetting.

Surface preparation and other types of coatings inspection are normally performed by third-party inspection organizations. Surface preparation is the most important part of any coatings application project, and inspection by NACE or Norwegian FROSIO (the Norwegian Professional Council for Education and Certification of Inspectors for Surface Treatment)-certified inspectors is often required. These third-party inspectors are trained to insure that surface preparation and coatings applications are conducted in accordance with established international standards as specified by the coatings inspection and application contract. Inspectors with this training are also involved with evaluation of existing coating systems to determine the extent of coating damage and recommend remedial measures.

**Surface Cleaning** Neither abrasive blasting nor water jetting can remove grease and other organic surface contaminants. These problems must be removed with various commercial products suited to this purpose.

Soluble salts may also be present on the metal surface. They are not removed by abrasive blasting, and can lead to osmotic blistering of newly applied coatings.<sup>9</sup> Chloride salts are normally removed by water washing or water jetting, often with proprietary chemical additions sold for this purpose added to the water. It is common to check for the presence of soluble chlorides by various methods, and most coatings contracts will specify a maximum level of acceptable chloride contamination on the surface. The amount of chlorides detected will vary depending on the detection method, and the method should be specified in the coatings contract.

While chlorides are not the only soluble salt contamination found on metal surfaces, washing that removes chloride salts will normally remove any other salty contaminant that could cause coating degradation and lack of adhesion.

**Abrasive Blasting** Abrasive blasting is the most commonly specified method of preparing steel surfaces for protective coatings.<sup>10</sup>

Tables 6.1 and 6.2 provide comparisons on the relative costs of abrasive blasting and other surface preparation methods. While the best surface preparation produces the longest-lasting coatings, the reduction in costs associated with less thorough surface preparation techniques can be significant.

The choice of surface preparation techniques and the necessary levels of cleanliness for new construction depend on the generic type of primer (chemical nature of the binder), severity of the environment, and the desired coating service life. Coatings should be applied in accordance with manufacturer’s recommendations, and these recommendations should include surface preparation guidelines listing minimally acceptable surface preparation conditions. General guidelines for selected generic coatings are shown in Table 6.3. The NACE/SSPC surface preparation standards are listed in Table 6.4. Note that while white metal blast cleaning, NACE No. 1/SSPC-SP 5, is the cleanest possible substrate for any of the coating systems, it is only required for IOZ primers. Substantial cost savings can be achieved if the surface preparation requirements for these other coatings are relaxed, but these savings are achieved at reduction in long-term performance of the coating.

All of the NACE/SSPC standards contain the following sections:

- Procedure before blast cleaning
- Blast cleaning methods and operations
- Procedure following blast cleaning
- Inspection

**TABLE 6.1 Comparative Costs of Different Surface Preparation Techniques<sup>9</sup>**

Surface Preparation	Cost	Performance	Dust	Debris
White Metal	100%	100%	100%	100%
Near White	80%	90–95%	100%	80%
LP WC	10%	70–80%	0%	3–5%
UHP WJ	25%	90%	0%	5–10%
Wet abrasive to white metal	120–150%	95%	0%	110–125%

Low Pressure Water Cleaning (LP WC) is cleaning performed at pressures less than 5000psi (34MPa). Minimum pressure is 3500psi; the use of a rotating tip is mandatory. Hand scraping of blisters and other defect may be required. Chemical decontamination is mandatory.

Ultrahigh Pressure Water Jetting (UHP WJ) is cleaning performed above 25,000psi (170MPa); the use of a rotating tip is mandatory. Chemical decontamination is mandatory.

Wet Abrasive Blast Cleaning to White Metal: Cleaning to SSPC SP 5, White Metal Blast Cleaning, use of water ring for dust control is mandatory. Chemical decontamination is mandatory.

**TABLE 6.2 Comparison of Abrasive Blasting Costs for General Construction**

Blast Method	Relative Cost
NACE #1 White Metal Blast	100%
NACE #2 Near White Metal Blast	70%
Commercial Blast, SSPC#6/NACE#3	40%
Brush Blast—loose rough previous coat	20%

**TABLE 6.3 Minimally Acceptable Surface Preparation Levels for Selected Generic Coatings**

Generic Coating Type	Recommended Minimum Surface Preparation
Alkyds and oil-based coatings	NACE No. 3/SSPC-SP 6 Commercial Blast Cleaning
Water-borne acrylics	NACE No. 3/SSPC-SP 6 Commercial Blast Cleaning
Epoxy	NACE No. 3/SSPC-SP 6 Commercial Blast Cleaning
Zinc-rich epoxy	NACE No. 3/SSPC-SP 6 Commercial Blast Cleaning
Inorganic zinc	NACE No. 1/SSPC-SP 5 White Metal Blast Cleaning

**TABLE 6.4 NACE/SSPC Joint Surface Preparation Standards**

NACE No. 1/SSPC-SP 5	White Metal Blast Cleaning
NACE No. 2/SSPC-SP 10	Near-White Metal Blast Cleaning
NACE No. 3/SSPC-SP 6	Commercial Blast Cleaning
NACE No. 4/SSPC-SP 7	Brush-Off Blast Cleaning
NACE No. 5/SSPC-SP 12	Surface Preparation and Cleaning of Metals by Water Jetting Prior to Recoating
NACE No. 6/SSPC-SP 13	Surface Preparation of Concrete
NACE No. 8/SSPC-SP 14	Industrial Blast Cleaning
NACE No. 10/SSPC-PA 6	Fiberglass-Reinforced Plastic (FRP) Linings Applied to Bottoms of Carbon Steel Storage Tanks
NACE VIS 7/SSPC-VIS 4	Guide and Visual Reference Photographs for Steel Cleaned by Water Jetting
NACE VIS 9/SSPC-VIS 5	Guide and Reference Photographs for Steel Surfaces Prepared by Wet Abrasive Blast Cleaning

Inspections of blast-cleaned surfaces include measurements of the surface profile. If a surface is too smooth, the primer will not develop adequate bonding to the substrate. If it is too rough, the coating may be too thin at high spots and pinpoint corrosion may occur. Figure 6.5 shows the rough surface and anchor pattern of a blast-cleaned pipeline prepared for recoating.

**Water Jetting** Water jetting is currently used primarily for preparing surfaces for recoating. The reason for this limitation is because most water jetting systems cannot

produce an adequate surface profile or anchor pattern. This limitation has been largely overcome, but water jetting is still used much less than abrasive blasting for coatings surface preparation.<sup>12</sup> The NACE/SSPC surface preparation standards listed in Table 6.4 describe water jetting only for recoating purposes. This is shown in Figure 6.6, where water jetting is being used for surface preparation on the outside of a large marine vessel prior to recoating.

The advantages of water jetting, which uses high-pressure water, are that it removes most contaminants,



**Figure 6.5** The surface of a pipeline ready for recoating in the field.



**Figure 6.6** Water jetting surface preparation prior to recoating. Photo courtesy of Hammelmann Corp., Dayton, Ohio, reproduced with permission.

has no sparking or dust hazards, and removes soluble salts. Corrosion inhibitors are sometimes added to the water to prevent flash rusting, although opinions differ on how deleterious these thin rust areas are to primer-to-metal adhesion.

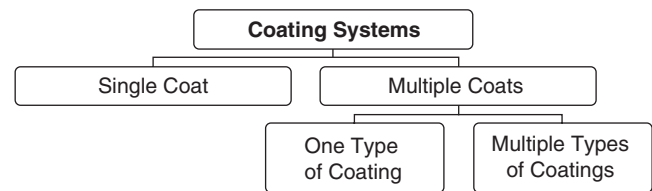
Table 6.5 provides approximate comparisons between water jetting and abrasive blast cleaning standards.

### Purposes of Various Coatings

Protective coating systems usually consist of multiple layers of paint having different purposes, but some

**TABLE 6.5 Comparison of Water Jetting and Abrasive Blast Cleaning Standards and Surface Conditions**

Surface Finish Grade	ISO 8501-1	SSPC	NACE
White metal	Sa 3	Sp 5	No. 1
Near-white metal	Sa 2½	SP 10	No. 2
Brush-off	Sa 1	SP 7	No. 4
Solvent cleaning		SP 1	
Power tool cleaning	St 2 or 3	SP 3 <sup>34</sup>	
Power tool cleaning to bare metal		SP 11	
HPWJ and UHPWJ		SP 12	No. 5
WJ-1 clean to bare substrate			
WJ-2 very thorough or substantial cleaning			
WJ-3 thorough cleaning			
WJ-4 light cleaning			
Wet abrasive blasting		TR 2	6G198



**Figure 6.7** Single and multicoat protective coating systems. Photo courtesy of NACE International, reproduced with permission.

systems are intended to be single-layer coatings or multiple layers of the same type of coating. These choices are shown in Figure 6.7.

The various layers of a coating system must be compatible with each other, and this is normally done by using the same coating manufacturer for all the layers, typically primer, intermediate, and topcoat.

A single coat system is usually a relatively thin system and usually provides minimal protection appropriate for temporary protection during shipping and manufacturing. These single-film coatings are often referred to as “shop coats” and should be replaced before service in any aggressive environment. Some single-film systems are much thicker, such as the trowel-applied coating shown in Figure 6.8, which is used for protection of girth welds after welding in pipeline construction. Other single-film coatings are sometimes applied as maintenance coatings in the splash zone where surface preparation is difficult and thick films are necessary, and interfilm adhesion is difficult to achieve. Problems with





**Figure 6.8** Trowel application of thick-film single coating of coal-tar urethane for field application at pipeline girth welds. Photo courtesy of NACE International, reproduced with permission.

single-coat systems include solvent entrapment in thick systems, difficulty maintaining desired coating thickness, and potential holidays and misses.

Multiple-coat systems can be layers of the same product or a variety of products that combine the desired properties of each layer, for example, primer, barrier intermediate coat, and topcoat.

Coatings are classified in two different ways. Some classifications specify coatings by binder chemistry, for example, epoxy and polyurethane. The chemistry of these binders is understood by coatings manufacturers and many field-oriented coatings professionals. Most field-oriented coatings professionals do not understand the chemistry of coatings; they just know what works, and what does not work. Coatings manufacturers list their products by generic binder types or by appropriate applications.

### Generic Binder Classifications

**Alkyd Paints** These paints provide minimal protection and are seldom used in oilfield applications. Note that many manufacturers will call these systems paints to distinguish them from the more protective chemistries listed as “coatings”—implying *protective* coatings.

**Bituminous Coatings** These asphalt or coal-tar-based coatings are seldom used in oilfield applications on metal substrates with the exception of field-applied repairs and girth-weld coatings on buried pipelines. At one time, coal-tar coatings were standard coatings for pipelines and other oilfield structures, but environmental and occupational health concerns have limited their use in recent years.

**Vinyl Coatings** Vinyl coatings are widely used protective coatings for corrosion resistance in chemical service. They are easy to apply and form tight homogeneous films over the substrate. Intercoat adhesion is also excellent. They do soften slightly when covered with some crude oils. Their flexibility allows them to accommodate the motion of the steel substrate, for example, during ship or platform launching.<sup>13</sup>

They are physically drying, one-component paints, and usually cannot withstand temperatures greater than 75–80°C (165–175°F). They are relatively easy to apply and quick drying, but they have low solids content and have relatively high VOC contents.

Film thickness is typically only 50µm (2mils), and this, combined with their relative softness, means they cannot withstand mechanical abuse. It also limits their use on rough, previously coated surfaces.

**Chlorinated Rubber Coatings** Chlorinated rubbers were once widely used for marine and other oilfield applications,<sup>13</sup> but worker safety and environmental concerns have limited their use in recent years.

**Epoxy Coatings** These coatings are the workhorses of the marine coatings and oilfield industries. Most epoxies require near-white blast coating surface preparation, although some versions can be applied underwater as repair coatings. With proper surface preparation, they have excellent substrate adhesion combined with good impact and abrasion resistance, and can achieve high film thicknesses.

Epoxies chemically cure. They are available in systems where the reactants are mixed during application as well as single-component products, which require more careful shipping and storage control and careful consideration of application and curing temperatures. These chemical-curing-related considerations mean that the use of epoxy coatings requires highly trained and experienced coatings contractors.

A wide variety of end-product properties can be achieved by varying the components, and epoxies are sold as pure epoxies, phenolic epoxies, coal tar epoxies, solvent-free epoxies, water-borne epoxies, and so on.

All epoxies are subject to UV degradation. This means they must be topcoated for most atmospheric exposures.

**Epoxy Mastic Coatings** These coatings have been marketed in recent years as easy-to-apply, inexpensive thick-film coatings. They have relatively short service performance compared with other coatings. Because of this, and the fact that coating materials are minor costs (approximately 10%) of coatings applications projects, their reduced cost is not justified for many applications.

They are not generally recommended for atmospheric or marine exposures, but they may be appropriate for buried service, for example, as repair coatings on pipelines.

**Acrylic and Polyurethane Coatings** These coatings are usually used as colored topcoats over epoxy-based primers and intermediate coatings. They have excellent hardness and very good UV and chemical resistance. They are two-component systems that require temperature and other application controls. The choice between various topcoats is often determined by pot life, application conditions, and curing time before they can be used.

**Polyester Coatings** Glass flake-reinforced polyester high-build coatings are used for high wear and abrasion applications such as walkways and the tidal and splash zones of steel structures.

**Vinyl Ester Coatings** These coatings find their best uses as tank linings. They are often applied as thick coatings (two coats of 750 $\mu$ m—30 mils, total 1500 $\mu$ m—60 mils). Many linings are applied as sheet materials, but these linings can be applied by airless spray as two-component liquids that quickly cure. Glass flake reinforcement improves abrasion resistance. They should only be applied over blast-cleaned steel (NACE No. 2/SSPC-SP 10).

**IOZ Coatings** IOZ coatings have metallic zinc pigments. They are widely used as primers for long-lasting atmospheric exposure protection. They are not generally recommended for buried or submerged service.

The zinc pigments make mechanical contact with each other and with the steel substrate. This allows them to provide galvanic protection of exposed steel at holidays, and they usually have at least 75% by weight metallic zinc in the dry film.<sup>5</sup> The precise minimum zinc content for effectiveness depends on which of several commercially available inorganic binders is used.

IOZ primers will become dull gray upon weathering and sometimes require topcoats for visibility or color coding purposes. These topcoats reduce the effectiveness of the cathodic protection provided by the underlying IOZ primer. Unlike organic primers, IOZs are immune to UV degradation, so sunlight exposure is never a problem, and many IOZ primers with no topcoats have been used for decades with minimal degradation.

Surface preparation for IOZ primers requires at least a commercial blast cleaning (NACE No. 3/SSPC-SP5), but white metal blasting (NACE No. 1/SSPC-SP 5) is preferred and will result in better performance. Topcoating of IOZ primers requires cleaning to remove any reaction products that may have formed.

**TABLE 6.6 Comparison of Inorganic Zinc and Galvanized Coatings**

Inorganic Zinc	Galvanizing
Not a metallic coating	Metallic coating
Excellent corrosion resistance	Excellent corrosion resistant
Chemically bonded to steel substrate	Chemically bonded to steel substrate
Individual particles	Continuous zinc
Medium abrasion resistance	Limited abrasion resistance
Slower reaction with acids	Faster reaction with acids
Long life span	Shorter life span

Table 6.6 compares the performance of IOZ and galvanizing coatings.

For all but the most benign environments, for example, onshore atmospheric exposures, galvanizing is not practical, at least in part, because of the thin coatings applied by standard commercial galvanizing operations.

Zinc is an amphoteric metal, and it corrodes at unacceptable rates in both acids and bases. This means that no zinc-coating pigments can be used for direct exposure to acids, for example, drilling muds and many other completion and workover fluids, or to bases. Topcoats are necessary in these environments.

**Organic Zinc Primers** Organic zinc primers are used for many of the same applications as IOZ primers. Their organic binders mean that, unlike IOZ coatings, organic zinc primers must be topcoated to protect them from UV degradation. The organic binder also means that the cathodic protection provided by the metallic zinc pigments is less effective, because the intermetallic contacts between the pigment particles and between the pigments and the steel substrate are less effective due to the resistivity of the organic binder.

IOZ primers are fast drying and their overcoating interval is relatively short. They are compatible with all of the topcoat systems used in oilfield applications. Problems occur with alkyds, but they are seldom used in oilfield applications due to their limited environmental resistance.

Organic zinc primers are used to recoat and spot paint over IOZ and galvanizing.

The surface preparation for organic zinc primers requires at least a near-white blast cleaning (NACE No. 2/SSPC-SP 10), and they are less tolerant of surface salts than IOZ primers.

**Polyurea Coatings** Polyurea coatings show much promise and will become more prevalent in the future. The advantages of polyureas include their quick setting,

insensitivity to ambient temperature and weather changes during application, and good mechanical properties. Unfortunately, their quick-setting properties limit their adhesion to metal substrates, and they are not currently used as protective coatings for large metal structures. It is likely that these limitations will be overcome, and polyureas will become standard protective coatings for many oilfield applications when that happens.

### Coatings Suitable for Various Service Environments or Applications

Several organizations suggest appropriate coatings systems for various environments and applications. Tables 6.7 and 6.8 show the SSPC classification of environments and suggested coatings systems for these environments.<sup>14</sup> Norsok, the Norwegian standards organization, recommends the coating systems for offshore platform applications shown in Table 6.9. The referenced publications also contain suggestions on surface preparation methods and the necessary surface conditions prior to coating application.<sup>7,14</sup>

**TABLE 6.7 SSPC Environmental Zones<sup>14</sup>**

Zone	Description
0	Dry interiors
1A	Normally dry interiors
1B	Normally dry exteriors
2A	Frequent wetting by fresh water
2B	Frequent wetting by salt water
2C	Immersion in fresh water
2D	Immersion in salt water
3A	Acidic atmospheric exposure, pH2–5
3B	Neutral chemical atmospheric exposure, pH5–10
3C	Alkaline chemical atmospheric exposure, pH10–12
3D	Atmospheric exposure with solvents and hydrocarbons
3E	Severe chemical atmospheric exposure

Many coatings manufacturers and suppliers list the coatings by application instead of by generic type. These listings generally follow terminology similar to that shown in Tables 6.6–6.8, and they often specify the recommended operating temperatures (usually as maximum acceptable sustained temperatures) that the coating systems can withstand. Coating systems from various manufacturers will perform differently, and it is common to test new coatings systems for performance in accordance with recommended accelerated exposure testing procedures.<sup>15</sup>

### Coatings Inspection

Surface preparation and other types of coatings inspection are normally performed by third-party inspection organizations. Surface preparation is the most important part of any coatings application project, and inspection by NACE or Norwegian FROSIO (the Norwegian Professional Council for Education and Certification of Inspectors for Surface Treatment)-certified inspectors is often required. These third-party inspectors are trained to insure that surface preparation and coatings applications are conducted in accordance with established international standards as specified by the coatings inspection and application contract. Inspectors with this training are also involved with evaluation of existing coating systems to determine the extent of coating damage and recommend remedial measures.<sup>16</sup>

Documentation of coatings inspection is very important, because the third-party inspector must convince all interested parties that the surface preparation, coatings application, and inspections have all been conducted in accordance with contract requirements and industry standards.<sup>17</sup> Owners want perfect coatings and contractors want payment; these conflicting interests must be resolved in accordance with pre-agreed procedures. Written standards, for example, NACE, SSPC, and ISO take preference.

**TABLE 6.8 Selected Environmental Zones for which SSPC Systems Are Recommended<sup>14</sup>**

Painting System		Environmental Zone											
SSPC #	Generic Type	0	1A	1B	2A	2B	2C	2D	3A	3B	3C	3D	3E
PS 11	Coal tar epoxy				x	x	x	x	x	x	x		
PS 12	Zinc rich (no topcoat)		X	X	X	X	X	X		X		X	
PS 12	Zinc rich (with topcoat)		X	X	X	X	X		X	X	X	X	
PS 19	Ship bottoms												
PS21	Ship topsides		X	X	X	X							
CS 23	Metallic thermal spray		X	X	X	T	X	T	T	T	T		

T, recommended only with proper sealing or topcoating.

For zone 3E, use specific exposure data to select a coating.

**TABLE 6.9 Recommended Coating Systems for Various Locations on Offshore Platforms<sup>7</sup>**

Application	Coating System	NDFT (μm)
Carbon steel	1 coat zinc-rich epoxy	60
Operating temperature <120°C	1 coat two-component epoxy	200
Structural steel	1 coat topcoat	75
Exteriors of equipment, vessels, piping, and valves (not insulated)	MDFT (μm)	335
All carbon steel surfaces in noncorrosive areas (e.g., living quarters)		
Deck areas		
Carbon Steel	Thermally sprayed aluminum or alloys of aluminum	200 min
Operating temperature >120°C		
All insulated surfaces of tanks, vessels, and piping		
Flare booms	Sealer	
Underside of bottom deck, jacket above splash zone, crane booms, lifeboat stations are optional stations		
Walkways, escape routes, and other deck areas as specified	Nonskid epoxy screed	3000
Under epoxy-based primer	1 coat epoxy primer	50
	or	
	1 coat zinc-rich epoxy	60
	1x epoxy tie coat	25
	MDFT (μm)	85
Under cement-based fire protection	1 coat zinc rich epoxy	60
	1 coat two-component epoxy	200
	MDFT (μm)	260
Application (if not specified in others)	1 coat epoxy primer	50
Uninsulated stainless steel when painting is required	1 coat two-component epoxy	100
Aluminum when painting is required	1 coat topcoat	75
Galvanized steel	MDFT (μm)	225
Insulated stainless steel piping and vessels at temperatures <120°C	2 coats immersion grade epoxy phenolic	2 × 150
	MDFT (μm)	300
Submerged carbon steel and carbon steel in the splash zone	1 coat epoxy primer <sup>a</sup>	225
	1 coat two component epoxy	225
Submerged stainless steel and stainless steel in the splash zone	MDFT (μm)	450
Internal seawater filled compartments, e.g., ballast tanks		

<sup>a</sup> NORSOK states “two component epoxy for both layers.”

Common inspection hold points or checkpoints include:

- Pre-surface inspection
- Post-surface preparation
- Pre-painting
- During and after application

The initial surface inspection determines the condition of the steel surfaces before operations begin. The ISO standards for degree of rusting serve to indicate the relative initial surface condition before surface preparation and coatings begin.<sup>18</sup>

- A—Steel surface largely covered with adhering mill scale but little, if any rust
- B—Steel surface has begun to rust and from which the mill scale has begun to flake
- C—Steel surface on which mill scale has rusted away or from which it can be scraped, but with slight pitting visible under normal vision
- D—Steel surface on which mill scale has rusted away and on which general pitting is visible under normal vision

Each type of paint coating will have a specific surface preparation requirement that must be followed.



Proper paint adhesion depends on the removal of all greases and other organic contaminants prior to surface preparation. Abrasive or water jetting cannot be relied upon to do this, so solvent cleaning is usually necessary to remove them. This contamination is normally detected visually, but UV (black) lighting is sometimes used to aid in organic contaminant detection.<sup>12,19</sup>

The presence of soluble salts on metal surfaces has been recognized for many years as leading to premature coatings failures. These salts are normally chlorides and sulfates, but other species may also be present. They are usually removed by power washing. Proprietary commercial products claim to aid in this salt removal. Chloride contamination receives most of the soluble salt attention, and any washing process that removes chloride salts is likely to also remove other salts.

No internationally recognized standards on the acceptable levels of salt contamination on a metal surface are available, although efforts are underway to develop them. Table 6.10 shows the limits suggested by NACE for offshore structures. These levels are to be measured using methods suggested by ISO standards.<sup>20,21</sup>

One of the problems with soluble salt detection and measurement is the wide variability associated with measuring the salt levels on rough surfaces. Replication is difficult. One promising method of diminishing this variability is the development of conductometric testing. Instead of using colorimetric titrations or similar methods of determining the salt content on a metal surface, the surface can be exposed to a source of deionized water, and the resulting conductivity can be measured as a direct indication of the soluble salts that are present. This method has the added benefit of measuring all salts, not just chloride ions.<sup>20-24</sup> Steel surfaces must have a profile in order for the paint coatings to develop

adequate surface contact and adhesion. This is one of the main results of abrasive blasting and is considered to be a limitation to many water-jetting operations. If the surface profile is too deep, paint films will not adequately cover the highest points, and pinpoint rusting will occur. This idea is shown in Figure 6.9. Pinpoint rusting is unsightly, but it can also lead to eventual undercutting and wider corrosion problems. The surface profile necessary to insure adequate bonding and to avoid pinpoint rusting will depend on the type of coating involved.

Anchor patterns and surface-profile determinations are usually evaluated visually by placing laboratory-prepared optical comparators on the surface and comparing the adjacent abrasive-blasted surfaces to the comparator. Figure 6.10 shows one version of commer-

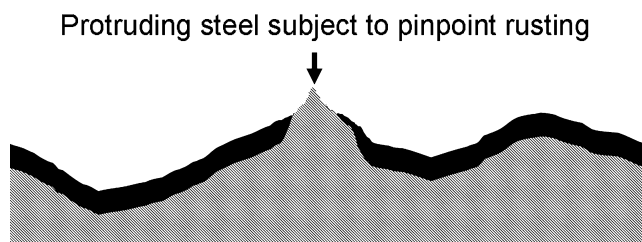


Figure 6.9 Protruding steel subject to pinpoint rusting.

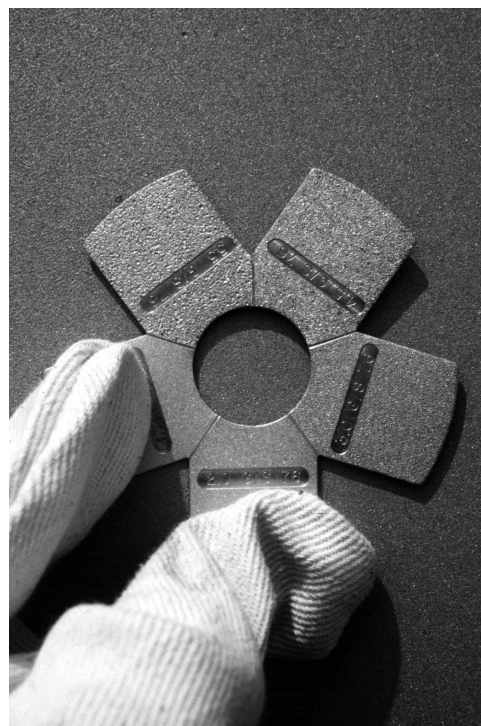


Figure 6.10 Keane-Tator surface-profile comparator disc. Photo courtesy of KTA-Tator, Inc., reproduced with permission.

**TABLE 6.10 Recommended Maximum Allowable Total Soluble Chloride Ion Contents for Offshore Structures<sup>12</sup>**

Coating Category	New Construction	Maintenance
Splash zone, exterior submerged zone, and ballast water tank	20 mg/m <sup>2a</sup>	20 mg/m <sup>2a</sup>
Atmospheric zone	20 mg/m <sup>2</sup>	50 mg/m <sup>2</sup>
Stainless steels	20 mg/m <sup>2</sup>	20 mg/m <sup>2</sup>

Nace RP 0108-2008 table 15, reproduced with permission.

<sup>a</sup> The level of residual salt contamination on the surface has a very significant effect on the service life of the immersion-type coating systems. A clean surface should be obtained prior to coating. However, if the soluble chloride ion content is high and obtaining a clean surface is too costly, the allowable soluble chloride ion content shall be agreed to by the coating applicator and facility owner.

cially available comparators used for this purpose. Comparisons are made with a specially constructed magnifying glass that allows comparison of the surface in question with four different grades of surface preparation. Other methods of surface-profile determination include the use of replica tape for making a negative image of the surface in question. A soft plastic tape with a hard backing is applied to the area in question. After the tape is removed, the profile of the tape replica is measured using a specially calibrated microscope.<sup>14,25-30</sup>

Coating inspectors also use visual photographs available from NACE and SSPC to document the surface conditions to be expected after wet abrasive blasting or water jet cleaning.<sup>31,32</sup>

The appearance of grit-blasted surfaces will vary depending on the specific grit used and the steel substrate in question. It is often advisable to prepare a field sample for referee purposes prior to starting a surface preparation project. This field sample, representative of the agreed-upon surface cleanliness for the project, may be a plate of metal or a part of the structure. These prepared areas can then be used as reference by the contractor and the inspector. It is important that the surface be preserved in its “as agreed” condition until the project is completed.

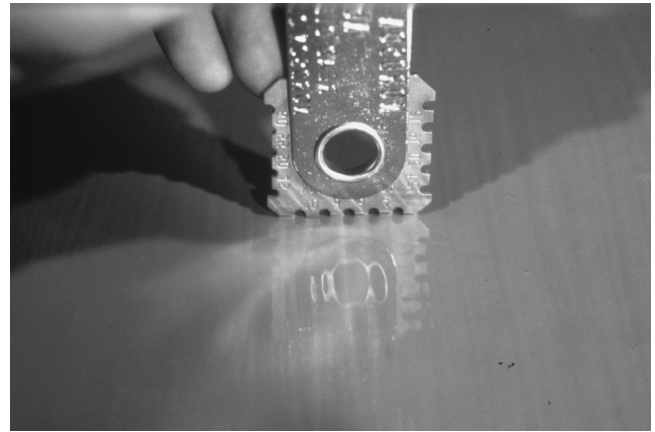
### **Inspection Before and During Coating Application**

Application equipment and methods need to be inspected prior to and during painting operations. This includes making sure that pigments are stirred and suspended in the vehicle, proper mixes of two-component paints are maintained, and so on. New low-VOC paints make coating application more difficult and harder to apply.

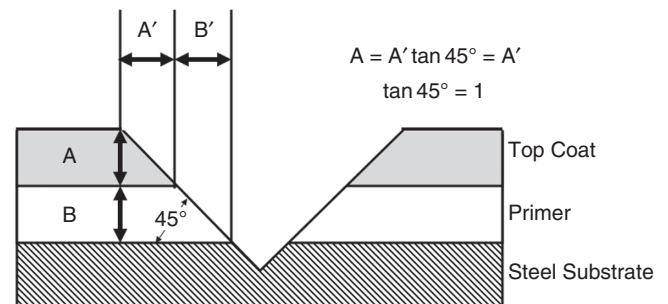
Pigments need to be stirred and suspended in the vehicle. Proper operation of all equipment must be insured so that the coating will be delivered in the appropriate manner.

The newer low-VOC paints make coating application more difficult and increase the need for better coatings inspection.

Wet film thickness is normally determined manually by inserting a special tool into the wet film as shown in Figure 6.11. The notches between the teeth on this tool have various depths, and the wet film thickness is determined as the midpoint between the last coated notch and the next deeper notch. Once the thickness is measured, the wet film will usually flow back and cover the tooth marks. The dry film thickness can be estimated by knowing the percent solids in the paint, and corrective action can be taken to reapply more paint or reduce the application rate as needed. Thin films will not provide adequate coverage, and many thick films will not cure correctly. If a more precise measurement is necessary,



**Figure 6.11** Wet-film step or notch gage applied to a newly painted surface. Photo courtesy of NACE International, reproduced with permission.



**Figure 6.12** Cross section of a coating cut for Tooke gage measurement of dry film thicknesses.

eccentric roller gages, lens gages, or needle micrometers can be used.<sup>33</sup>

**Inspection after Application** The most common tests applied to dry films are thickness and adhesion measurements.

Magnetic thickness gages are usually used for dry-film thickness determinations on steel substrates. They need to be calibrated, and they are less accurate on curved surfaces or thin (sheet vs. plate) carbon steels.<sup>34,35</sup> They usually cannot be used on most stainless steels with the exception of the low-alloy 13-chrome martensitic stainless steels used for pipelines and similar applications, where they must be specially calibrated to compensate for the reduction in magnetic alpha ferrite in the metal.

Nondestructive magnetic measurements can be confirmed by destructive tests, which are also used in cases of disputes. The most common destructive test uses a Tooke gage, which measures the exposed cut coating after it has been cut with a special scribe.<sup>36</sup> The exposed cut surfaces, shown in Figure 6.12, are viewed under a

special magnifying glass, and the thickness of the cut edges are calibrated on the instrument.

Adhesion tests are nondestructive tests often performed on dry films in accordance with a variety of international standards.<sup>37–39</sup>

Coating holidays are defects (usually holes, which may be microscopic) in the coating that expose the underlying metal to the corrosive environment. They are normally detected using electrical holiday detector. An electrode is passed over the surface being inspected and, as it passes over a defect, the system passes current between the electrode and the metal being inspected.<sup>40</sup> The operator can then mark the holiday for repair. This is shown in Figure 6.13. While Figure 6.13 shows the inspection of an internal coating in a large diameter pipe, the same procedure is used on structural metal, pipeline exteriors, and any steel structure coated with a nonconductive coating system. Holiday detectors must be selected for the appropriate application, as high-voltage detectors used on thick-film exterior pipeline coatings would damage thinner coatings, and the lower-voltage instruments used for thin films would not penetrate thicker, more resistant coatings.<sup>40,41</sup>

Any defects noted during surface preparation, application, or after film drying should be noted and remediated before the next step in the coatings or construction process.

**Weather Conditions** Weather conditions must be measured before coatings operations can begin. Table 6.11 shows the conditions where condensation will form on a metal surface depending on the metal temperature, air temperature, and relative humidity. NORSOK specifies that no final blast cleaning or coating applications



**Figure 6.13** Electrical holiday testing in the interior of a large-diameter water pipe.<sup>11</sup> Photo courtesy of NACE International, reproduced with permission.

**TABLE 6.11** Relative Humidity and Surface Condensation Temperatures on Uninsulated Metal Surfaces<sup>42</sup>

Metal Surface Temp.	Surrounding Air Temperature °F																
	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120
35°F	60	33	11														
40		69	39	20	8												
45			69	45	27	14											
50				71	49	32	20	11									
55					73	53	38	26	17	9							
60						75	56	41	30	21	14	9					
65							78	59	45	34	25	18	13				
70								79	61	48	37	29	22	16	13		
75									80	64	50	40	32	25	20	15	
80										81	66	53	43	35	29	22	16
85											81	68	55	46	37	30	25
90												82	69	58	49	40	32
95	% of Relative Humidity												83	70	58	50	40
100													83	70	61	50	
105														84	70	61	50
110															85	71	61
115																85	72
120																	86

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R. Baboian, *NACE Corrosion Engineer's Reference Book*, 3rd edition, NACE International, Houston, TX, 2002, p. 74, reprinted with permission.



can be conducted if the relative humidity is greater than 85%, the steel temperature is less than 3°C (5°F) above the dew point, and coating applications and curing temperatures must be above freezing for both air and metal temperatures.<sup>7</sup> This Norwegian standard is primarily intended for the cold and humid conditions found in the North Sea and nearby construction yards. NACE recommends air temperatures above 5°C (40°F) and relative humidities of 85%. Some paints can be applied at lower temperatures and moisture-cured urethane coating systems may be used at higher humidities.<sup>12</sup> Coatings must always be applied in accordance with the manufacturer's recommendations, and some coatings, for example, epoxies, may require higher temperatures for proper curing.

### Areas of Concern and Inspection Concentration

This section is intended to illustrate a number of practices necessary to insure successful coatings applications, inspection, and repair. In any structure there are areas where coatings surface preparation, application, and repair are more difficult. There are also regions on a structure where corrosion damage, if encountered, will be more significant than the unsightly damage elsewhere on the same structure. These are areas that can sometimes be remediated prior to coating. If they cannot, then special attention must be paid during all phases of a coating project, as well as during operations when the difficult/critical areas should require additional emphasis.

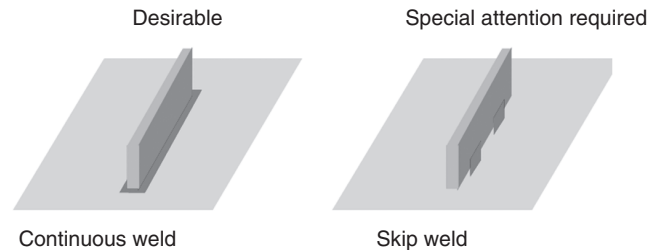
**Key Features that Should be Remediated Before Coating** There are certain features, perhaps structural defects, on structures that should be removed before surface preparation and coating application. Several of these are shown in Figures 6.14–6.17. These features should be removed or minimized before surface preparation begins; otherwise, they will lead to premature coatings failures.<sup>43</sup>

Skip welds are often applied to hold equipment in place during construction and usually supply adequate strength for structural purposes. Unfortunately, if they are not sealed using continuous sealing welds, they allow crevices to form. This is a major problem for any struc-

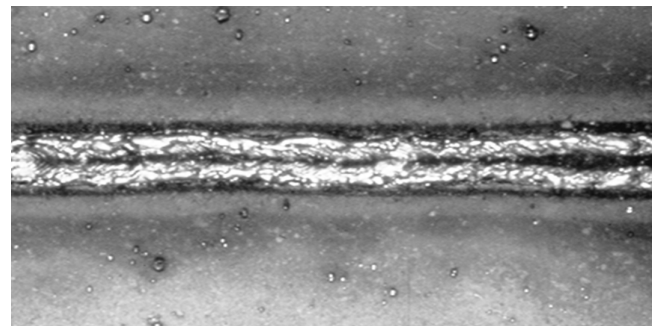
ture intended for immersion service, but crevices allow moisture to collect and create corrosion problems even in atmospheric exposure. The sealing welds do not need to be strong, because this could cause metal distortion, as shown in Figure 4.22, but they should be water tight and inspected to insure that no cracks or crevices remain.

Welds should be ground smooth and weld splatter should be ground flat so that it does not cause thin layers or bare spots in the coating.

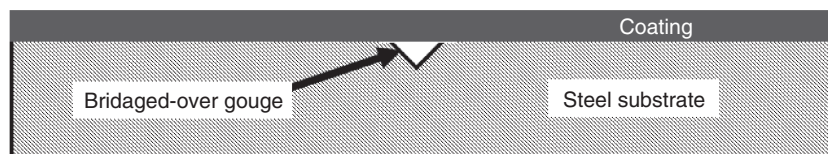
Voids due to bridged-over gouges or coating shrinkage will collect moisture, especially in immersion service, and will eventually lead to coating failure. The sharpness of the gouges or internal corners should be ground smooth or, in the case of internal corners like those shown in Figure 6.17, a rounded weld bead can increase the radius and provide more surface area for adhesion.



**Figure 6.14** Skip welds versus continuous welds. Drawing courtesy NACE International, reproduced with permission.

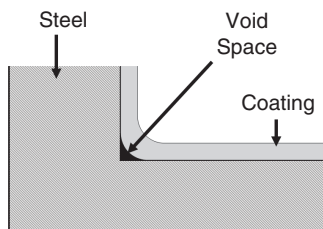


**Figure 6.15** Weld splatter. Drawing courtesy NACE International, reproduced with permission.

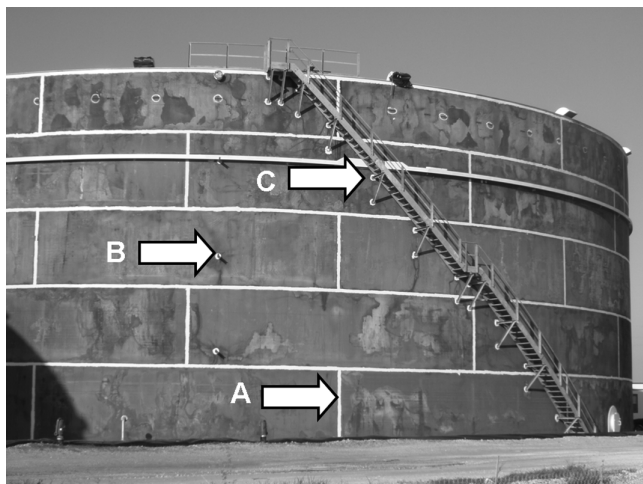


**Figure 6.16** Gouge with bridged-over coating subject to moisture accumulation and corrosion.





**Figure 6.17** Void space caused by coating shrinkage.



**Figure 6.18** Stripe coating prior to painting on an above-ground storage tank: (a) welds; (b) through-wall fitting; and (c) ladder attachments.

**Stripe Coating** Certain key locations will remain difficult to clean, coat, and inspect. It is common practice to use stripe coatings in these locations. A stripe coat is a supplemental coating applied to ensure there is adequate protection of critical areas like flanges, edges, welds, and so on.<sup>7</sup>

Stripe coats are shown in Figure 6.18 on an above-ground storage tank under construction. They should be allowed to set-to-touch before overcoating.

Stripe coats are usually applied by brush or roller to insure adequate thickness. Their color should contrast with the substrate and with the overcoat to allow for easy inspection to insure adequate cover. It is considered good practice to grind all edges and to extend the striping at least 1 in. (2.5 cm) from the edges. This is especially important for maintenance coating, because exposed edges are more susceptible to corrosion and are likely to exhibit intergranular exfoliation (Fig. 6.19).

Construction aids, such as shown in Figure 6.20 must also be stripe-coated. While they are designed to be removed, they are often left in place.



**Figure 6.19** Flange on the exterior of an above-ground storage tank. All corrosion was ground away and the edges were rounded before abrasive blasting and stripe coating.



**Figure 6.20** Construction aid on an offshore structure tank wall that was left in place and stripe coated prior to overcoating.

Figure 6.21 shows equipment at a tropical pipeline receiving station with corrosion on fasteners, flanges, welds, and edges. All of these areas need to be ground smooth and stripe-coated after surface preparation is completed.

**Final Comments on Inspection** Most North American organizations use NACE, ASTM, and SSPC standards for coatings inspection, while European and other organizations tend to use ISO standards, which are likely to be derived from standards originally developed in



**Figure 6.21** Corrosion on a complicated geometry structure needing grinding and smoothing plus stripe coating after surface preparation.

European countries. This practice is changing, and the trend toward the use of ISO standards is likely to continue.<sup>17</sup>

While standard industrial practice is to develop and maintain checklists of items to be inspected, these checklists do not substitute for inquisitive and intelligent inspection teams. Unanticipated situations are likely to occur on many projects, and it is the responsibility of the inspection organization to bring them to the attention of the appropriate parties.

### Linings, Wraps, Greases, and Waxes

Internal linings, exterior wraps, and greases and waxes find limited but important uses as oilfield coatings.

**Linings** Linings are relatively thick coatings (paint layers) or, more commonly, sheet materials adhered to or in intimate contact with the interior surface of a pipe or other container. Their purpose is usually to protect the metal surface from corrosion, although some tubular product liners are also used to minimize flow resistance and increase production rates—usually on downhole tubing where inside diameters are restricted and boundary layer effects are significant.<sup>44,45</sup>

Linings are often used on tank bottoms and the lower interior side walls of large storage tanks as well as on cargo and product holds on ships, floating production storage and offloading vessels (FPSOs), etc. They are also used for lining pipelines, injection wells, production tubing, and other equipment tubular products.<sup>44</sup> Figure 6.22 shows a lining inside a flanged pipeline segment.



**Figure 6.22** The flange end of a liner segment installed in an oilfield pipeline.<sup>46</sup>

High-density polyethylene (HDPE) is the most commonly used liner material, but other thermoplastic materials are also used. HDPE liners are used for water injection pipelines and injection well tubing, for multiphase oil and gas gathering lines, sour multiphase crude product pipelines, and oil transmission lines. Medium-density polyethylene (MDPE) is used for water disposal and injection lines, while polyamide 11 (PA-11), also known as nylon, finds use for elevated temperature sour gas and multiphase sour hydrocarbon gathering lines.<sup>44</sup> Table 6.12 compares the relative costs of several resins used for lining offshore topside piping systems.

Many liners are used to prolong the life of existing structures that have already deteriorated significantly. This makes surface preparation difficult, but the surfaces to be lined should be as clean and as obstruction free as possible. A sizing plate is often run through the pipeline to confirm the minimum ID within the host pipe. Solid liners are then often inserted by pulling them through the system using an arrangement similar to that shown in Figure 6.23. Once the liner has been inserted, it is expanded against the liner wall, usually by fluid pressure. Most liners are thermoplastics, and they will set after a certain time, conforming to the restraints of the structure surrounding them.

It is important that liners fit tightly because gases, water, and other fluids will permeate all polymers and can accumulate at the liner-metal interface. Debonding of the liner can occur if the fluid pressure in the system is suddenly released and the accumulated gas pressure between the liner and the wall does not permeate through the liner. Venting systems have been developed

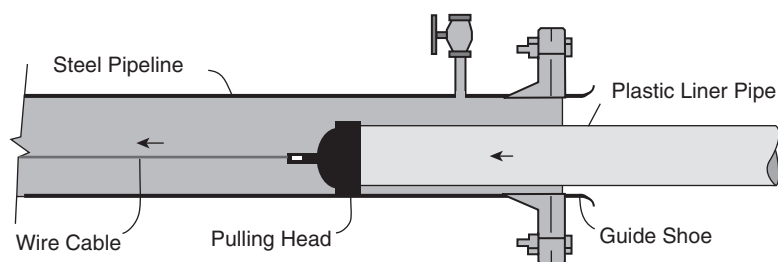
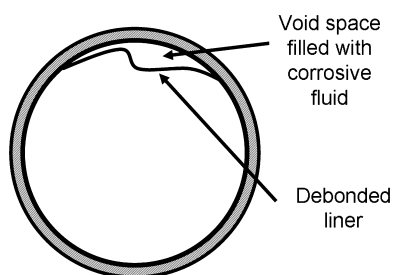
**TABLE 6.12 Common Water Analysis Determinations**

Determination	Produced Water and Other Waters	Injection Water	Cooling Water	Boiler Water
Alkalinity	X	X	X	X
Microbiological	X	X	X	
Barium		O		
Calcium	X	X	X	O
Carbonate	X	X	X	X
Carbon dioxide	X	O	O	X
Chloride	X	X	X	X
pH	X	X	X	O
Hydrogen sulfide		O		
Iron	X	X	X	O
Magnesium	X	X		O
Manganese	O			
Oxygen		O	O	O
Phosphate			O	O
Silica	X	X		X
Specific gravity	X	X	O	
Specific resistivity	X	X	O	X
Strontium		O		
Sulfate	X	X	O	X
Sulfite		O		O
Total dissolved solids	X	X	X	X
Zinc			O	

Adapted from table 4.1.<sup>53</sup>

X, determination usually made.

O, determination occasionally made, for example, manganese counts to correlate with iron counts for corrosion monitoring.

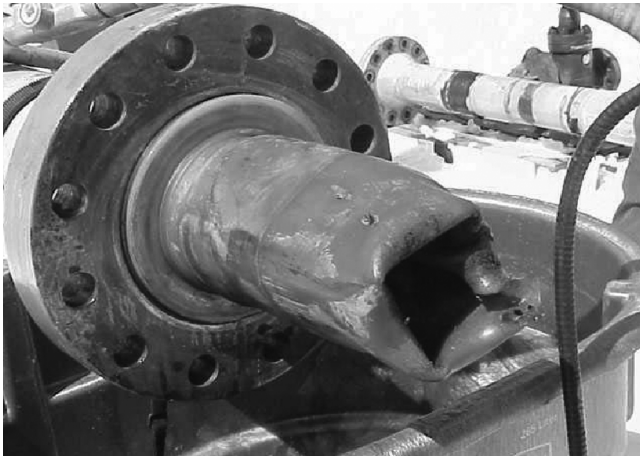
**Figure 6.23** System for drawing unexpanded liner into a pipeline.**Figure 6.24** Debonded liner caused by rapid pressure release in a fluid piping system.

to prevent high-pressure buildup in the annulus between the liner and the structure. If the proper venting does not occur, debonding such as shown in Figures 6.24 and 6.25 may result. Undetected debonding may allow corrosive fluid accumulation behind the liner. Debonded liners can also create significant flow restrictions.

Monitoring systems for checking the annular pressure behind linings have been noted. Through-wall X-rays can be used to identify precise locations where debonding has occurred.<sup>46</sup>

**Wraps** At one time, pipeline wraps were a standard means of coating the exterior of buried pipelines. Many years of field experience have shown that this is no





**Figure 6.25** In-service liner breach failure on a high-pressure sour gas pipeline.<sup>46</sup>



**Figure 6.27** Reinforced wraps used to coat flanges on above-ground piping systems.



**Figure 6.26** Petrolatum tape with glass-reinforced outer wrap used at the air-soil interface on piping. Photo courtesy of Denso, Inc.



**Figure 6.28** Plastic wrap on cooling tower piping. Photo courtesy of Denso, Inc.

longer advisable, because any motion of the pipeline is likely to produce debonding that will expose unprotected metal to the environment and also prevent cathodic protection from reaching the exposed substrate underneath the debonded wrap. The application of new long-distance pipeline wraps is now limited to occasional rehabilitation projects where the economics of wrapping is considered justified for short-term extensions on projected pipeline use. Wraps are still used extensively for many other applications, and some of them are discussed below. Other discussions appear in the section on pipelines later in this book.

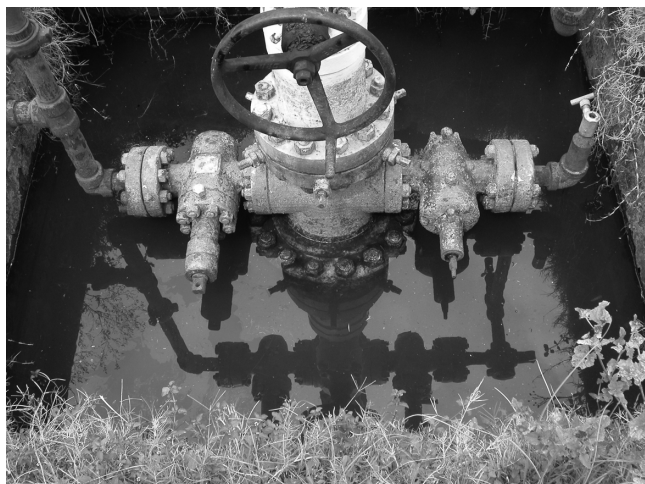
Figure 6.26 shows the application of wraps at the soil-air interface on pipelines. This is a common area for corrosion problems because of mechanical stresses that

can degrade pipeline coatings and the lack of soil consolidation which prevents effective cathodic protection. The two-layer wrapping system shown in Figure 6.26 includes a mastic tape intended to insure watertight bonding to the primary coating system, a fusion-bonded epoxy (FBE). The lighter-colored outer wrapping is glass-reinforced for mechanical damage protection.

Wraps are also used to protect hard-to-coat areas such as the bolted flanges shown in Figure 6.27.

Reinforced plastic wraps are often used on rigid piping systems such as the cooling tower piping shown in Figure 6.28. These relatively brittle plastics should not be used on equipment subject to mechanical vibrations or large thermal excursions because they can crack and lead to moisture intrusion.





**Figure 6.29** Wet valves in a sump on a crude oil pipeline.

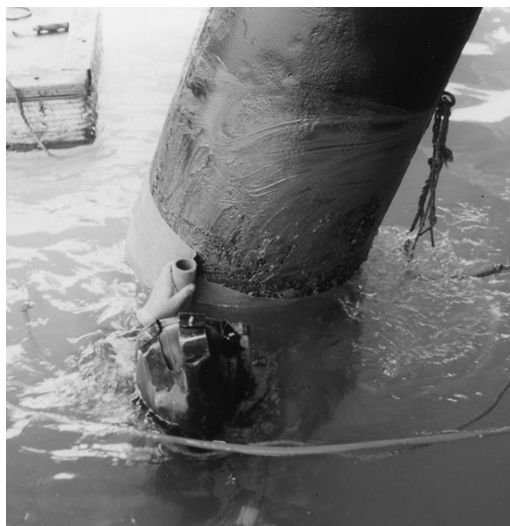


**Figure 6.30** Waxed tape on a valve in a manhole.

Many wet surfaces are so complex and their surface preparation is so difficult that no other coating systems are appropriate. Figure 6.29 shows valves in an outdoor sump associated with a tropical-climate crude oil pipeline. Wax-filled wraps like the ones shown in Figure 6.30 are the preferred means of controlling exterior corrosion in these situations. The reinforced wraps are intended to provide a diffusion barrier against moisture intrusion, and the hydrophobic nature of the wax filler further reduces water intrusion.

Another advantage of wraps is they can be applied to wet surfaces with minimal surface preparation. Figure 6.31 shows a swimmer applying a wrap to the underwater and tidal portions of a marine piling.

Most wraps are intended to be moisture permeation barriers, but if they are debonded or mechanically



**Figure 6.31** Repair wrap being installed on the tidal and splash zone portions of a marine piling. Photo Courtesy of Denso, Inc.



**Figure 6.32** Pitting of underground pipeline where wrap was ineffective in preventing corrosion.

damaged, they often act as electrical insulators preventing cathodic protection currents from reaching the exposed metal surface. This happened on the pipeline shown in Figure 6.32, and extensive corrosion occurred underneath the wrap.

It is important that wraps have sufficient mechanical strength and substrate adhesion. If they do not, they can unravel from the structure as shown in Figure 6.33.



**Figure 6.33** Low-build nonadhesive wrap coming loose from above-ground pipeline. Photo courtesy of S. Munoz, Corrosion y Proteccion, Cuernavaca, Mexico.

**Greases and Waxes** These materials are hydrophobic and are often used for temporary coatings to limit corrosion. Waxes are often incorporated into wraps to enhance their ability to limit moisture migration.

### Coatings Failures

All coatings will eventually fail. The reason for the following discussions is to provide some insight into why these failures occur. If they are the inevitable result of aging, then the coating system selection, surface preparation, and application were suitable for the intended service. If premature problems develop, understanding why these problems occurred will help coatings professionals decide how to prevent them in the future. This understanding may also provide useful information justifying more expensive surface preparation or inspection procedures. Surface preparation is usually the most expensive and most important part of any coating application, and corrosion professionals must frequently justify more expensive procedures to management.

Reasons for coating failures, in their approximate order of importance, are:<sup>12</sup>

- Poor surface preparation and cleanliness
- Poor coating application
- Poor or inadequate inspection
- Poor specifications (both construction and coating)
- Poor component design
- Murphy's Law

Remember, most coating systems will work for their intended environment and most coatings failures are

due to inappropriate surface preparation or application procedures or conditions.<sup>47,48</sup>

**Normal Aging Failures** Normal protective coating aging failures may show the following phenomena:

- Blistering
- Checking, alligatoring, or cracking
- Chalking and discoloration
- Lifting or undercutting of the paint film

Figure 6.34 shows a marine piling with typical aging of the protective coating. Several degradation processes are apparent.

Coatings inspectors are trained to evaluate coatings degradation in accordance with established international standards. Figure 6.35 shows one of many figures from ASTM D 610, one of the standards used to rate corrosion underneath protective coatings.<sup>49</sup>

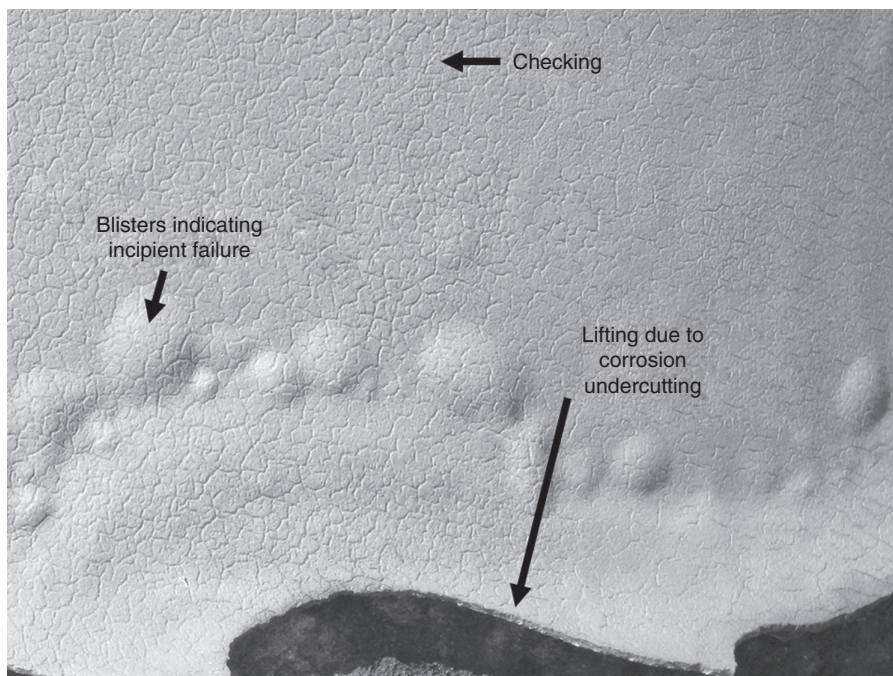
Blisters may be a normal result of aging coating systems or they may be early indicators of improper coating application.

All paint films are permeable to moisture to some extent. Blistering occurs when the moisture at the film-to-substrate interface builds up to the extent that pressure is exerted and the coating-substrate interface debonds. Water will always migrate through the paint film driven by osmosis, and when the osmotic pressure within the blister balances the coating adhesion around the blister circumference, the blister will cease to grow. Some blisters are associated with areas of corrosion, which may start at coating holidays, whether these are from the original coating process or due to mechanical damage after the coating has set and aged. Most blisters will show minimal corrosion beneath the blister due to the high pH of the water that collects in the resulting cavity. They should not be broken unnecessarily, because this will remove the protective paint film and allow more aggressive fluids to attack the underlying substrate. When blisters occur late in the lifetime of a coating, they are indications of imminent coating failure.

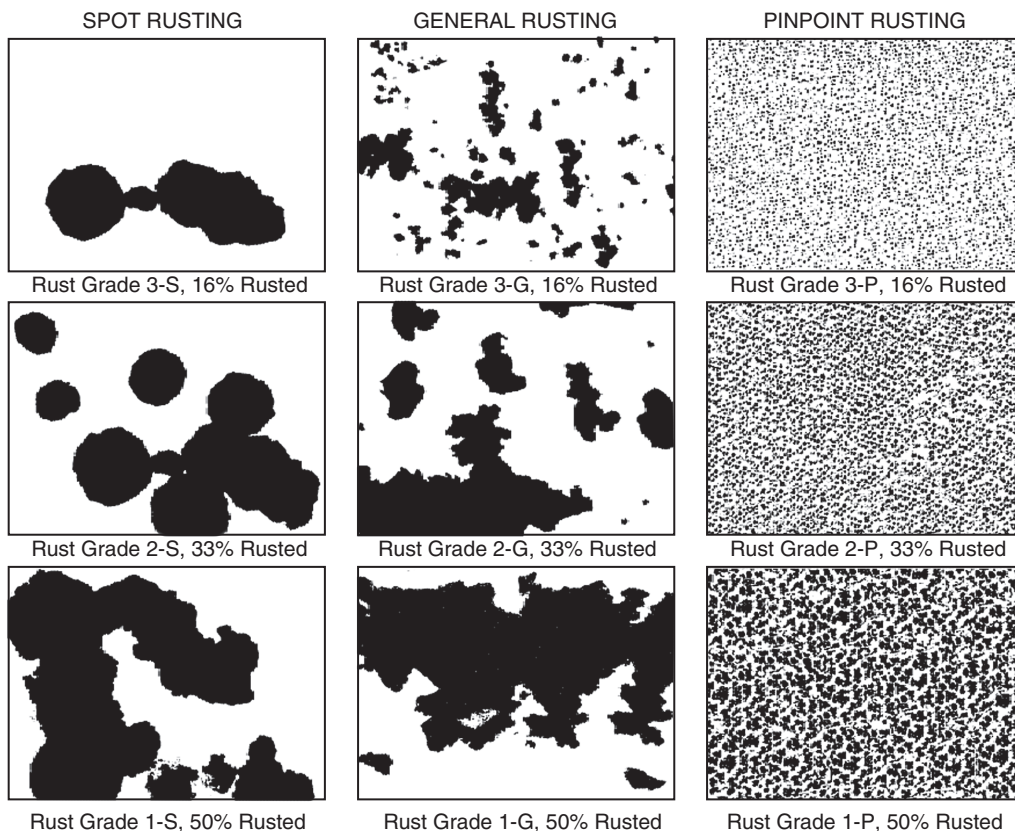
Figure 6.36 shows blisters on the below-ground section of a pipeline vent riser. One of the blisters has been broken to show the uncorroded steel underneath. If the soil had remained undisturbed by a construction project, the coating would have continued to provide corrosion protection for many more years.

Figure 6.37 shows blisters forming near a scratch on the exterior of a buried pipeline coating. Most of the coating is undamaged, but blisters are forming parallel to the scratch, and the coating would eventually debond and fail. The black spots in the blistered area are where the blisters have been broken to reveal discolored but otherwise uncorroded steel.

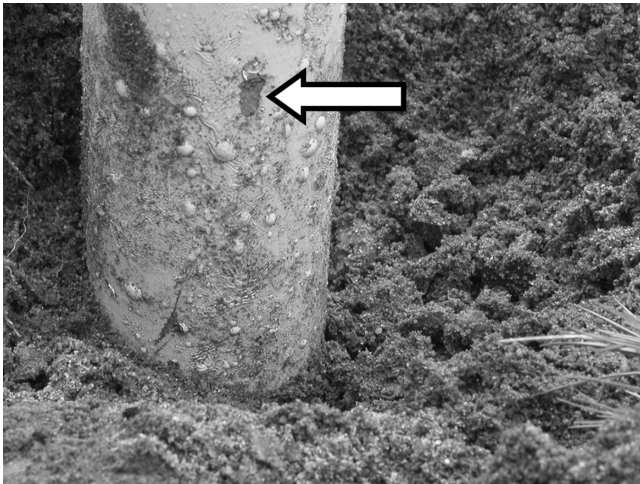




**Figure 6.34** Marine piling with aging coating showing typical aging features and patterns.



**Figure 6.35** Example of spot rusting pictures from ASTM Standard D 610.<sup>49</sup> Reproduced with permission of ASTM International.



**Figure 6.36** Osmotic blisters on a riser near the air–soil interface. The arrow indicates a location where a blister was broken for this photograph. Note the lack of corrosion beneath the blister.

Coatings inspectors evaluate blistered coating surfaces by comparing their appearance to published photographs in international standards. They then rate the frequency and size of blisters. Figure 6.38 shows one photograph used for this purpose.<sup>51</sup>

Checking, alligatoring, and cracking are terms that refer to similar phenomena; the only difference is the depth of penetration of the coating defects. They can be defined as follows:

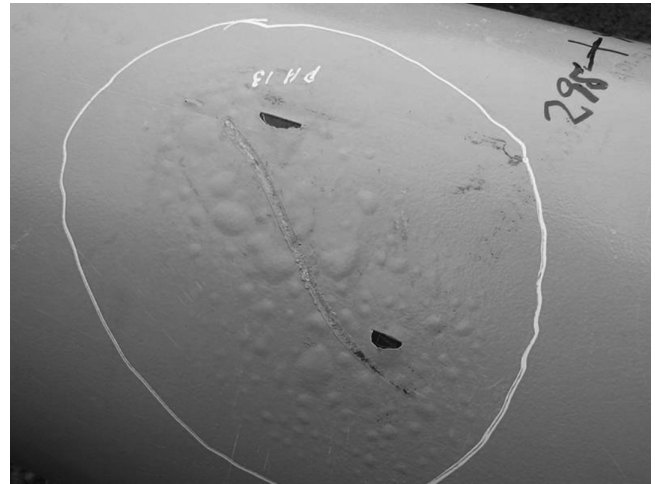
**Checking**—slight breaks in the surface film

**Alligatoring**—wide and extensive breaks in the surface. This is most common in bituminous pavements and other thick films, but it is also seen on oilfield equipment. The name is intended to indicate that the surface looks like an alligator's hide.

**Cracking**—breaks in the film extend to the substrate, which often leads to corrosion.

Checking, the least extensive of these phenomena, often occurs as a coating dries or continues to react. It can be an indication of a coating setting too quickly at elevated ambient temperatures. It also happens as coatings degrade, and degradation due to weathering, including UV degradation, starts to become significant on the coating surface (Figure 6.39).

A coarse checking pattern on the surface of a coating is sometimes called alligatoring. It is typically caused by aging, sunlight exposure, and/or the loss of volatile components as the coating sets and ages.



**Figure 6.37** Coating blisters forming around scratches on a pipeline coating. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

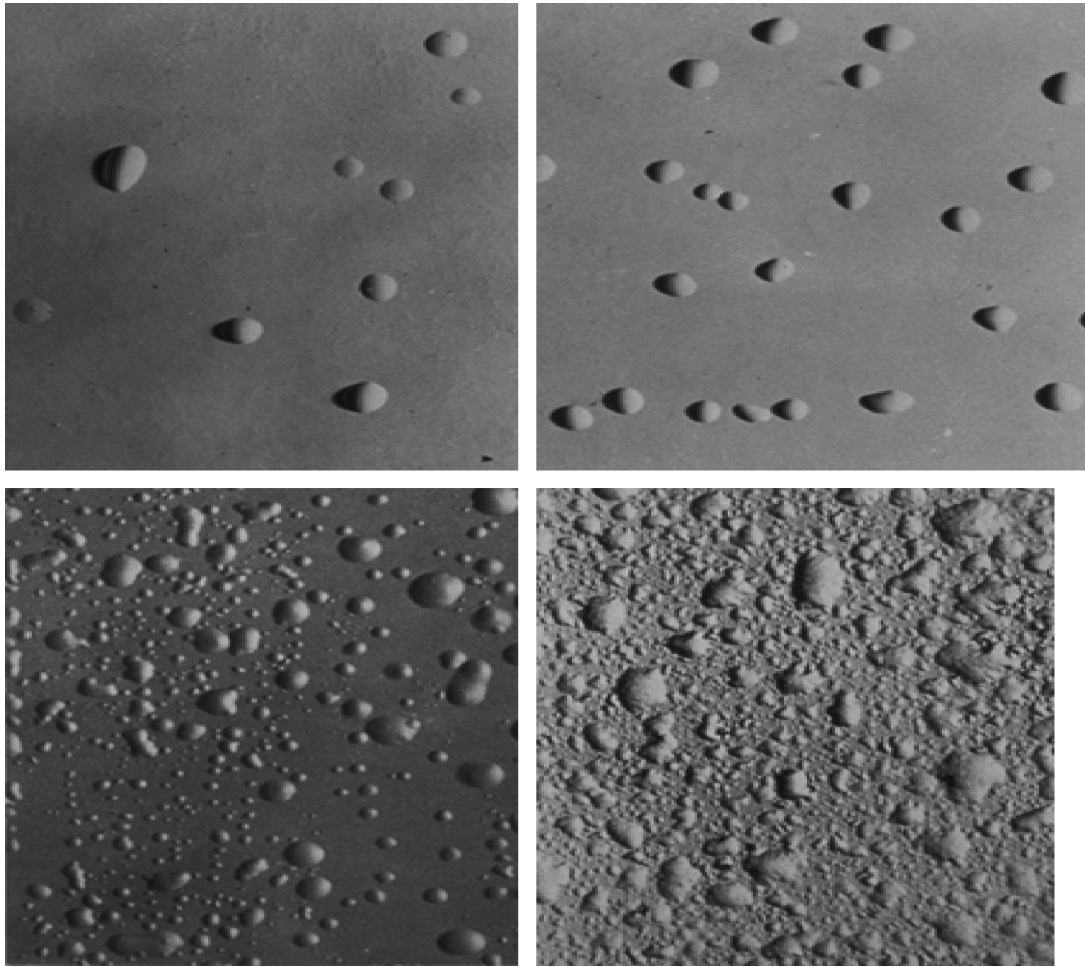
The wide and extensive breaks in surface films classified as alligatoring often occur when a hard, tough coating is applied over a softer, more pliable intermediate layer or primer. Some coatings, if applied too thickly, can alligator when exposed to sunlight. If the ambient temperature during curing is too high, the surface may cure rapidly compared with deeper portions of the same film and produce this effect (Figure 6.40).

The differences between checking and alligatoring are open to interpretation, but cracking, as used in the protective coatings industry, indicates that the surface defects extend to the substrate. This often leads to visible corrosion, as shown in Figure 6.41. The cracking shown in Figure 6.41 is due to the combination of an aging coating and the flexure of the substrate. This is common on many offshore platforms and similar structures.<sup>12</sup>

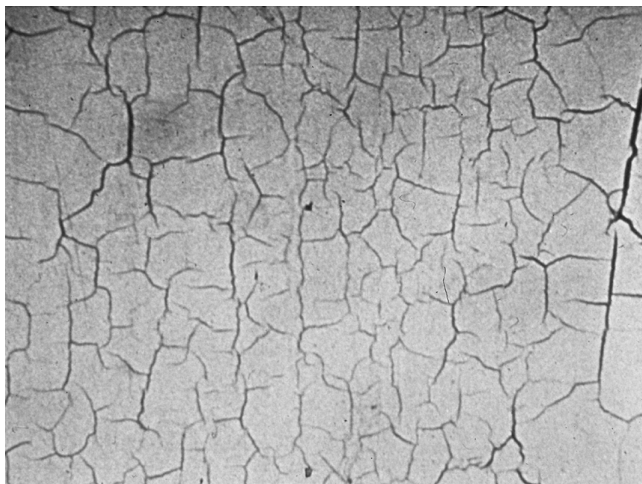
Lifting and debonding occur after corrosion starts, usually at holidays or cracks. As corrosion progresses, the increased volume of the corrosion products compared to the metal from which they are formed creates stresses and eventually lifts the protective film. This is shown at the bottom of Figure 6.34 and in Figure 6.42.

Chalking is the formation of a loose powder due to UV degradation of organic coating binders. This is shown in Figure 6.43. Epoxies are prone to this problem, and this is a reason why epoxies used for atmospheric exposure usually have non-epoxy overcoats. Another means of control is the use of inorganic pigments which are immune to UV degradation. Chalking is a sign of UV degradation, but it is normally only a cosmetic problem. If UV degradation continues, then checking or

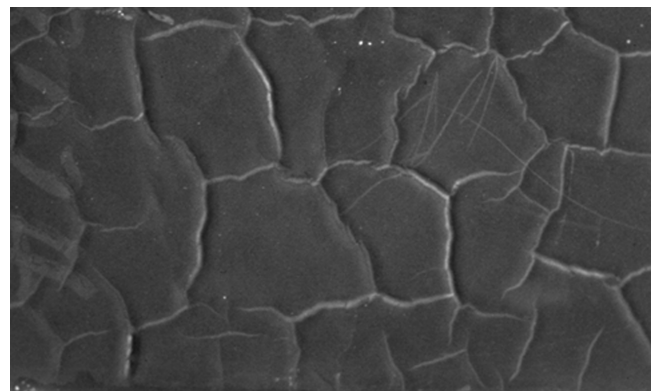




**Figure 6.38** Blisters from ASTM D714. From the upper left, these pictures show Size 2 blisters with few, medium, medium dense, and dense ratings.<sup>51</sup> Reproduced with permission of ASTM International.



**Figure 6.39** Checking on the surface of a protective coating. Reproduced with permission of NACE International.



**Figure 6.40** Alligatoring of a protective coating after many years of seaside exposure in a semitropical environment. Reproduced with permission of NACE International.



**Figure 6.41** Cracking due to structural motion on the exterior wall of a vessel. Note the rust staining at locations where motion has occurred and at welds.



**Figure 6.42** Protective coating lifting from the surface of a pipe due to corrosive undercutting. Photo courtesy of NACE International, reproduced with permission.

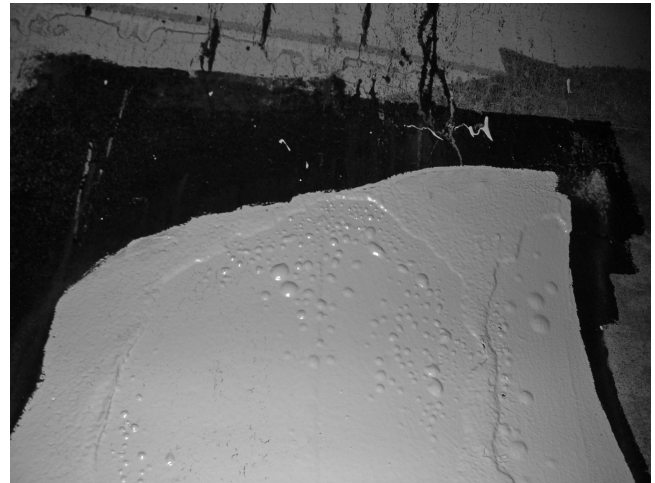
cracking may eventually occur. While it may be considered unsightly, it seldom indicates a lack of coating protectiveness.

**Failure Modes for New Coatings** It is important to recognize these forms of coating failure as they are indications of one or more of the following:

- Improper surface preparation—Organic solvents, salt contamination, or improper surface profile



**Figure 6.43** Superficial chalking on a coating surface. Photo courtesy of NACE International, reproduced with permission.



**Figure 6.44** Blisters formed on light-colored repair coating due to improper surface cleaning. Photo courtesy of NACE International, reproduced with permission.

- Incorrect application or curing temperature
- Paint application either too thick or too thin
- Incompatible coatings for the substrate (to include primers and undercoats)
- Improper coating for the service conditions. This usually takes time for indications to develop, but identification of this problem can prevent using the same system elsewhere in similar situations.

The blisters shown in Figures 6.34, 6.36, and 6.37 are the normal result of aging or mechanical damage to the protective coating system. Blisters can also form on newly applied coatings when gases or liquids are trapped underneath the coating at the coating-substrate interface. This is shown in Figure 6.44, where the light-colored



repair coating has extensive blisters, mostly on the bare metal surface, as opposed to the locations where this same repair coating has been applied over the existing coating.

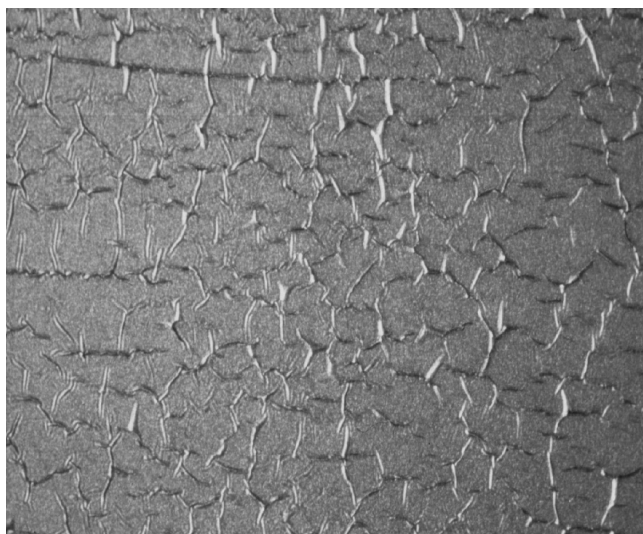
These blisters form due to soluble material in the coating leaching out of the paint film and becoming trapped at the paint–substrate interface. The outer surface hardens and becomes less permeable and the solvents become trapped. The presence of blisters on newly applied coatings is an indication of one or more of the following conditions:

- Improper surface cleaning prior to paint application. Contamination can be either organic greases and oils or soluble salts.
- Paint applied too thick to allow evaporation of the solvent or suspension vehicle.
- Solvents evaporating when the temperature increases
- This can be either organic contaminants or soluble salts

Wrinkling is the result of paint being applied too thick or too hot. The surface of the coating expands more rapidly as it dries than the inner portions of the wet paint film. Figure 6.45 shows a wrinkled surface.

Pinholes are small visible holes in coating caused by:

- The spray gun being too close to the surface, which can force bubbles into the coating
- Incorrect solvent balance in the coating

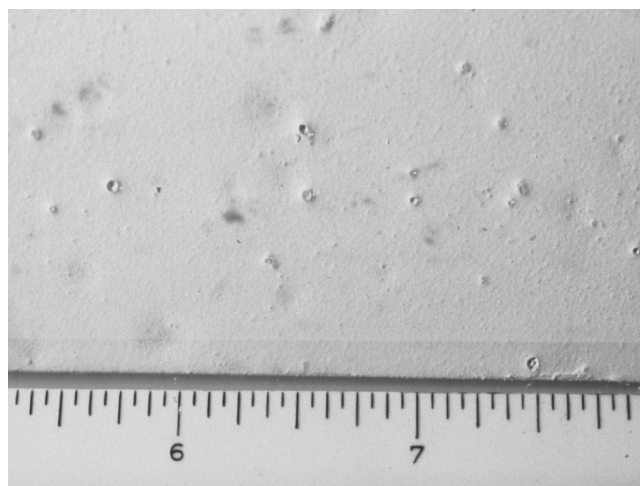


**Figure 6.45** Wrinkled paint surface. Photo courtesy of NACE International, reproduced with permission.

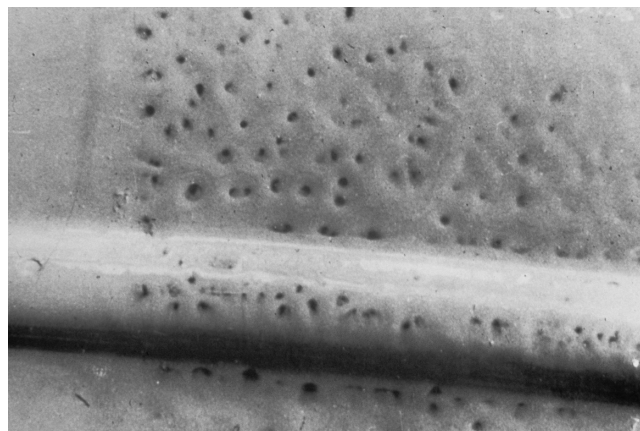
- Too volatile solvents
- Hot weld spatter

They are caused by a collapse of air or solvent vapor bubbles. Note how many of the pinholes in Figure 6.46 have craters around the edges.

Fisheyes look similar to pinholes; the difference is that they are caused by a lack of adhesion to the substrate. They are usually caused by improper surface cleaning or a lack of wetting of the substrate or particles in the paint (e.g., dust) by the paint film. The paint film pulls away from the contaminant leaving a tiny hole in the coating. The fisheyes shown in Figure 6.47 do not have the mounded rims shown for the pinholes in Figure 6.46.



**Figure 6.46** Pinholing on a coating surface. Photo courtesy of NACE International, reproduced with permission.



**Figure 6.47** Fisheyes in a coating. Photo courtesy of NACE International, reproduced with permission.

Conditions that lead to fisheyes include:

- Water or oil on the substrate surface
- Improperly formulated coating
- Converter not properly dispersed into the paint
- Incorrect thinning
- Incorrect spray technique
- Excess wet film thickness
- Application at low temperature

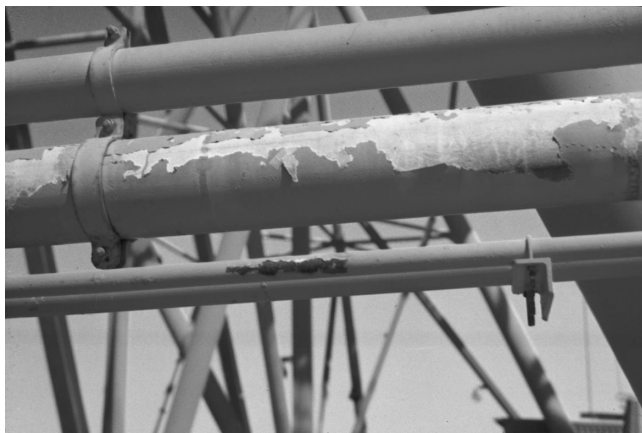
The heaviness of liquid coatings can cause sagging or runs, especially on vertical surfaces. Conditions leading to sagging and runs include:

- Excess wet film thickness
- Too much thinner
- Low temperatures
- Improper mixing

Delamination between paint layers and the loss of substrate adhesion in new coatings, where underfilm corrosion has not had a chance to initiate and progress, is due to incompatibilities between the overcoating and the substrate, whether the substrate is metal or another coating. This is a common problem with recoating projects and is shown in Figure 6.48.

Figure 6.49 shows mud cracking near a weld. These cracks can form in fairly new coatings as they dry and set. They occur in thick films and are a result of the wet film thickness being too great or of excessive thinning of the paint. As the film dries and shrinks, the cracks form. Early corrosion is a frequent result.

Overspray can look like abrasive dust on the surface of a coating and is poorly bonded to the coated surface.



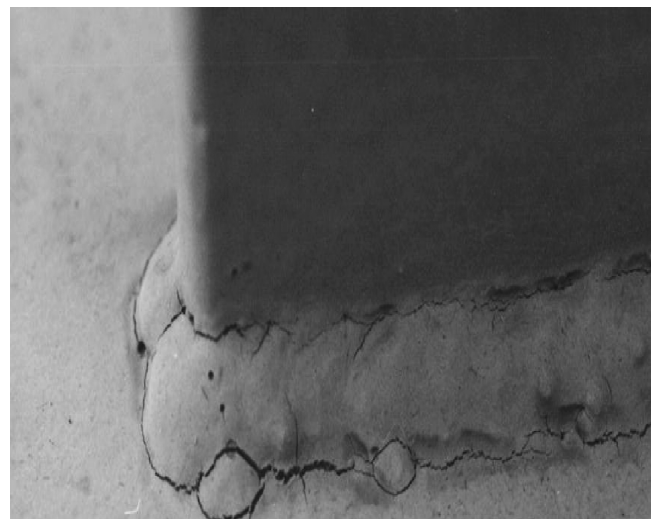
**Figure 6.48** Coating debonding. Photo courtesy of NACE International, reproduced with permission.

While unsightly, it is not a corrosion problem unless the oversprayed area is too thick.

Pinpoint rusting, shown in Figure 6.50, is the result of too little paint or of a too-rough surface profile.<sup>12</sup>

### Metallic Coatings

Metallic coatings find limited but important uses in oil and gas operations. The most commonly used metallic coatings are zinc, thermally sprayed aluminum, and corrosion-resistant metals and alloys such as chromium and electroless nickel. Zinc and aluminum are anodic to carbon steel in most environments, and they are more widely used. Chromium and other corrosion-resistant



**Figure 6.49** Mud cracking associated with a thick paint film around a weld. Photo courtesy of NACE International, reproduced with permission.



**Figure 6.50** Pinpoint rusting. Photo courtesy of NACE International, reproduced with permission.



metals are limited to smaller applications because of their relatively higher cost and because any coating holidays would produce an unfavorable area ratio and lead to accelerated galvanic corrosion.

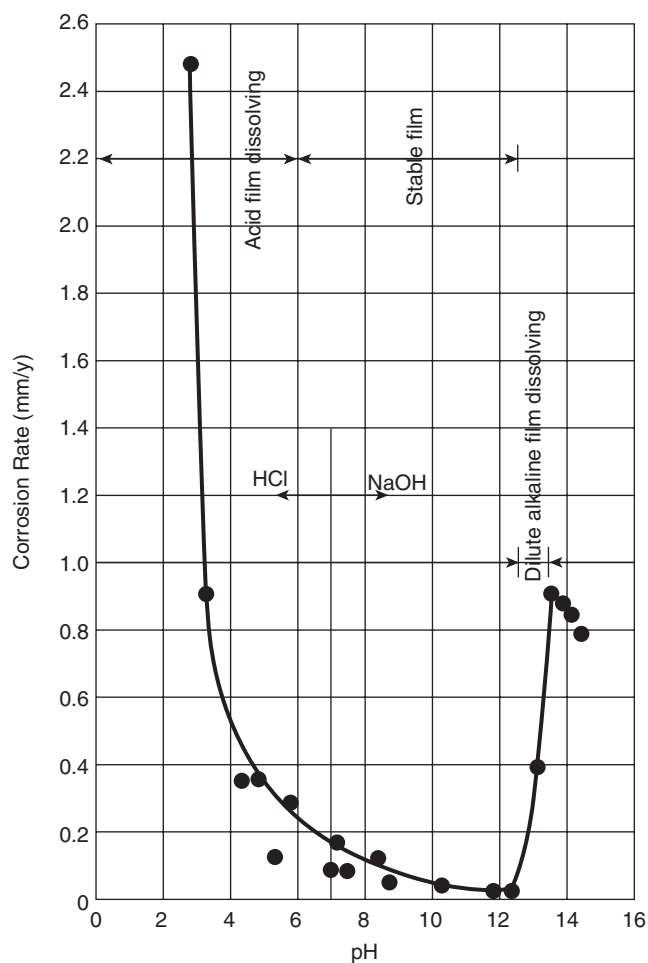
**Zinc Coatings** Galvanizing is a term usually reserved for zinc coatings applied to steel substrates by dipping the cleaned steel into molten zinc. The liquid zinc is sometimes alloyed to increase the fluidity of the liquid metal and to reduce the thickness of the zinc coating. Zinc is also applied by electroplating. The somewhat thinner zinc coatings produced by this method are preferred for threaded fasteners and other applications where close dimensional tolerances must be maintained. A third method of applying zinc is by Sherardizing, a method that deposits high-temperature zinc vapors onto the surface. This process produces zinc-iron intermetallic compounds on the surface, and this use is

usually restricted to complicated parts with interior geometries that are difficult to electroplate and cannot tolerate the somewhat thicker and less precise geometries obtained with hot dipping. Both electroplating and Sherardizing find their main uses on threaded fasteners and other close-tolerance applications.

Metallic zinc coatings are generally considered to be too thin and corrosion susceptible for use on offshore structures, but they are widely used for onshore structures and on some process equipment. Possible liquid-metal embrittlement of offshore structural metals and piping due to melted zinc in fires is another reason why the use of metallic zinc coatings offshore has been limited.

Zinc is an amphoteric metal, which means that it corrodes at unacceptable rates in both acids and bases. This is shown in Figure 6.51. The low corrosion rates in neutral atmospheres and in some neutral waters means that zinc coatings, which can be applied in factories during manufacturing processes, are attractive alternatives to painted coatings for many applications. If the zinc coating is breached, the nearby zinc corrodes to protect the nearby exposed steel. Eventually, the zinc is depleted and corrosion proceeds as shown in Figure 6.52. Note how the zinc coating is missing near the edges of the holes and where the metal is bent—two locations where coating holidays are likely to occur and corrosion will be accelerated.

While zinc is normally anodic to carbon steel, polarity reversals sometimes happen where zinc becomes anodic to steel. This only happens at temperatures greater than 60°C (140°F) in some freshwaters. The polarity reversal can lead to accelerated pitting at coating holidays in aerated fresh waters. This reversal is unlikely to occur in waters high in chlorides or sulfates.<sup>1</sup> The only other polarity reversal that has been reported



**Figure 6.51** Zinc corrosion versus pH of the environment.<sup>42</sup> Figure courtesy of NACE International, reproduced with permission.



**Figure 6.52** Corroded galvanized sign pole.

is tin becoming anodic to carbon steel in deaerated organic acids, for example, food “tin cans.”

Figure 6.51 was used to illustrate the idea that zinc is inappropriate for use in acidic or caustic (basic, high-pH) environments. Concerns about possible polarity reversal also limit use at elevated temperatures. The NACE standard for offshore coatings limits the use of hot-dipped galvanizing to temperatures below 60°C (140°F), presumably due to concerns about polarity reversal.<sup>12</sup>

Atmospheric corrosion of zinc coatings can also lead to hydrogen embrittlement of high-strength steels, and zinc coatings are not used on high-strength fasteners. ASTM A490 bolts, which have high hardness, should not have zinc coatings of any type because of this concern. Lower strength (hardness) bolts manufactured to ASTM A325 and ASTM A193 Grade B7 are acceptable for galvanizing according to most authorities.<sup>47,48,50</sup>

Galvanized structural steel is usually used with no top coating. If top coating is necessary, for example, for color coding or other purposes, special surface preparation precautions are necessary. If these precautions are not followed, debonding of the topcoat from the galvanized substrate can result. This is shown in Figure 6.53.

Coating defects can lead to premature corrosion on some galvanized structures. This is shown on the edges of a galvanized walkway landing alongside a large above-ground storage tank under construction. The spangle is still on the zinc coating, indicating that this rusting is very premature and due to coating defects present from the time of manufacture. Most coating holidays of this size on new construction are due to improper surface cleaning before placing the steel in the molten zinc bath (Figure 6.54).



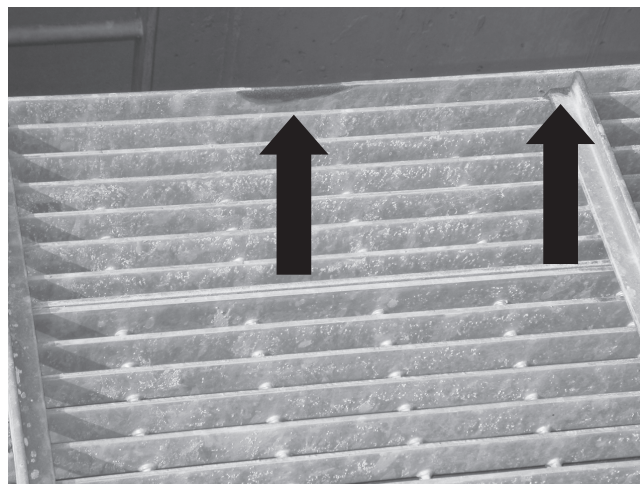
**Figure 6.53** Debonded coating on a galvanized pole.

**Thermal-Sprayed Aluminum (TSA) Coatings** TSA (also called flame-sprayed aluminum although there are non-flame processes as well) coatings are becoming more important for many applications. Tables 6.8 and 6.9 list several applications where TSA coatings are recommended. As experience with these coatings grows, it is likely that more applications will become apparent. They are currently recommended for various offshore applications and for corrosion under insulation in petrochemical piping.<sup>7,12,14,51</sup> TSA coatings work best when they are sealed with organic sealers or semiorganic silicone sealers.<sup>52</sup>

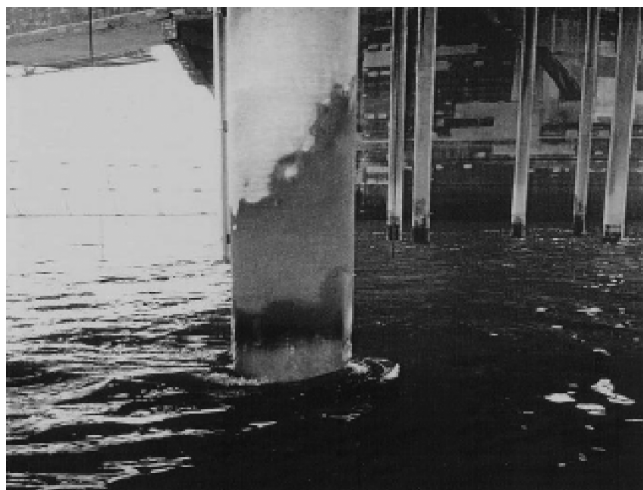
Conoco (now ConocoPhillips) has used TSA coatings for production risers since the mid-1980s. Most of this experience has been favorable, but problems have been reported, usually due to inappropriate TSA coating thickness, improper sealer application, or thermal cycling due to wave splashing and cooling.<sup>52</sup> Corrosion of hot risers and blisters due to inadequate sealing of TSA coatings are shown in Figures 6.55 and 6.56.

**Cadmium Plating** Electroplated cadmium was at one time the preferred metallic coating for bolts and other fasteners. The coatings are harder than similar electroplated zinc coatings and may be more corrosion resistant. Cadmium plating is still commercially available in North America, but environmental and occupational health concerns are limiting its use. Most organizations have stopped, or curtailed, the use of cadmium coatings, and the use of cadmium coatings is not recommended in recent NACE standards.<sup>12</sup>

**Amphoteric Coating Materials** Zinc, aluminum, and cadmium are often termed the amphoteric coating



**Figure 6.54** Premature rusting at coating defects on galvanized walkway.



**Figure 6.55** Corrosion of hot risers with improperly applied thermal sprayed aluminum coatings in the splash zone after only 2.5 years.<sup>52</sup> Photo courtesy of NACE International, reproduced with permission.

metals. All of them have unacceptable corrosion rates in acidic and basic environments.

**Chromium and Other Corrosion-Resistant Alloys (CRAs)** Chromium, nickel, and CRA coatings are used for corrosion resistance and also as hard facing for erosion resistance in many applications to include well-head equipment and pumps. In the absence of a reducible chemical, for example, oxygen or acid ions, little galvanic corrosion with nearby carbon steel is likely.

## WATER TREATMENT AND CORROSION INHIBITION

The most common classifications of water into types used in oil fields are:<sup>52</sup>

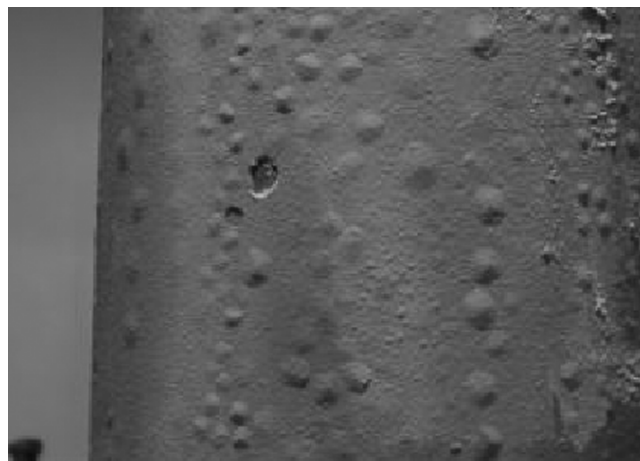
**Connate (Fossil) Water**—the original water trapped in the pores of a rock formation during its formation.

**Formation Water**—water present in the hydrocarbon-producing formation or related rock layers.

**Produced Waters**—these come from oil or gas wells and can be combinations of formation waters and condensates in various concentrations.

**Injection Waters**—these are surface waters injected into formations to maintain formation pressures. They contain dissolved solids and treatment chemicals.

**Condensed Waters**—these are waters that condense from the gas or oil well as temperatures and pres-



**Figure 6.56** Blisters on heated unsealed TSA aluminum.<sup>52</sup> Photo courtesy of NACE International, reproduced with permission.

ures change. These waters have low mineral contents and are often corrosive.

**Meteoric Waters**—these are waters that have come from surface sources and are normally in the upper layers of groundwater formations.

Connate, formation, produced, and injection waters are important to oil and gas production processes.

Surface waters are also classified by their salt contents into:

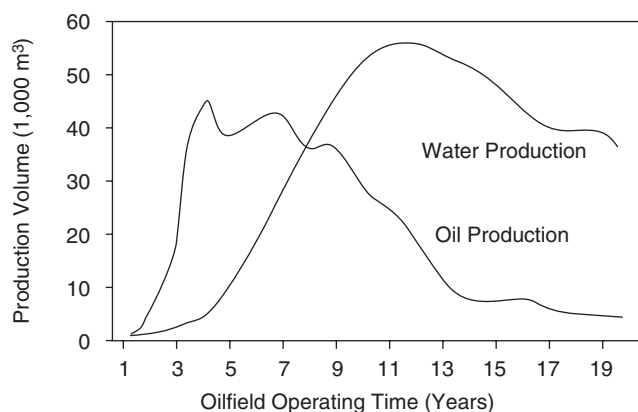
**Fresh Water**—low in salt content (<1000 ppm chlorides).

**Seawater**—found in oceans and seas, this water is usually about 3.5% sodium chloride plus significant concentrations of sulfate, magnesium, calcium, potassium, bicarbonate, and other ions.

**Brines**—have higher salt contents than typical seawater. Most oilfield waters fit into this classification.

**Brackish Waters**—these are found in bays, estuaries, and where major rivers empty into the sea. They are too salty to be considered freshwater, and their composition is intermediate between freshwater and seawater.

Injection waters are necessary to maintain formation pressure and to properly dispose of subsurface waters that have been separated from produced hydrocarbons. Many different source waters are used for injection including seawater, freshwater, and produced water. It is important to properly treat injection waters, because any



**Figure 6.57** Typical production profile for an oil field.<sup>53</sup>

oxygen, bacteria, or scale-forming minerals from the surface can cause souring or plugging of formations.

Figure 6.57 shows a typical production profile for an oil field. The water production continues to increase for several years after the peak oil production.<sup>53</sup> Worldwide, the water-oil-ratio (WOR) averages about three barrels of water for every barrel of oil, but the figures for the United States, where fields are older and production rates have declined, are approximately seven barrels of water for each barrel of oil. Higher WORs are still profitable. The annual costs of produced water disposal is estimated at US\$ 5–10 billion in the United States and as much as US\$40 billion worldwide.<sup>53</sup>

Oilfield waste water terminology has changed in recent years, and the following terms have been used since 2000:<sup>53</sup>

- Water-based muds (WBM) or fluids
- Organic-phase drilling fluids (OPF), which refer to liquids based on drilling fluids used when water-based fluids have been replaced by fluids necessary for directional drilling, horizontal completions, and other high-technology drilling techniques.

At one time, oilfield waters and brines were cleaned to 100 ppm oil and disposed into the ocean. Since 1960, U.S. state and federal regulations require all processed wastewater to be reinjected into the oil reservoir.<sup>53</sup> This trend has been followed elsewhere and has led to major increases in operating costs.

### Oil Production Techniques

Oilfield production can be classified as follows:<sup>53</sup>

**Primary Production**—uses reservoir energy to produce the oil and gas. The average recovery of

the oil in place is 12–15%, but this varies depending on the viscosity of the oil.

**Secondary Production**—water or gas injection produces an additional 15–20% of the original oil in place.

**Tertiary Production**—an additional 10–15% of the original oil in place is recovered using enhanced recovery techniques.

Note that these three stages only recover approximately 50% of the original oil in a formation. This means that as technology advances, more oil can be recovered from otherwise depleted reservoirs. Of course, the economics of this additional recovery depends on market conditions and the availability of other oil resources.

**Waterflooding** Waterflooding can lead to accelerated downhole corrosion and formation plugging due to scale formation. Injection water can mix with formation water. If this happens deep in the formation (below the water–oil boundary), this scaling may not have a significant effect on production rates.<sup>53</sup>

**Enhanced Oil Recovery (EOR)** There are a number of methods of EOR. Two of the more common methods are steam injection and CO<sub>2</sub> injection.

The terminologies for these various techniques are not universally applied, and it is common to use the term EOR for any recovery method that utilizes chemicals other than water for recovery. Secondary recovery is a term often used for repressurization of the reservoir with water or hydrocarbon-based gas to force oil out once the reservoir pressure has dropped.

Thermal processes usually involve heating the formation to reduce the viscosity of the unrecovered oil. The most common method is steam-assisted gravity drainage (SAGD), where hot steam is injected into the higher levels of the producing formation, and horizontal wells drilled at lower levels collect the oil and pump it to the surface. If steam is injected at excessive rates, the underground pressure and temperature can become too high and cause blowouts. Conversely, low temperatures will lower recovery rates.<sup>53</sup>

Steam injection often involves injecting low-quality steam (approximately 80% vapor and 20% water) into the formation to lower the viscosity of heavy oil in the formation. Provided the downhole formation is maintained below about 400°F (200°C), downhole corrosion is usually not a problem. Higher temperatures in the range of 500–700°F (260–370°C) create CO<sub>2</sub> and H<sub>2</sub>S problems, and the use of alloy tubular goods may become necessary.<sup>53</sup>

CO<sub>2</sub> injection, often termed miscible flooding, often involves injecting water after the gas in a process known



as water-alternating gas (WAG) recovery. This often produces aggressive corrosive environments with wet CO<sub>2</sub> and H<sub>2</sub>S and may require stainless steel or nickel alloys in selected locations.<sup>53</sup>

### Water Analysis

Complete water analysis is seldom necessary. Table 6.12 shows commonly performed water analyses for different purposes. Many of these determinations are performed by water-treatment companies that also provide chemicals for scale and corrosion control.

Several of these determinations, for example, all dissolved gas determinations and pH—which is influenced by dissolved gases—are pressure and temperature sensitive. This is the reason why most downhole pH determinations are calculated, and why some samples must be collected in pressure-maintaining devices. It is also important that analyses be done in a timely manner, as water chemistry may change significantly after samples are collected. Storage conditions cannot replicate the dynamic conditions of flowing fluids. Field measurements are especially important for pH, dissolved oxygen, and alkalinity.<sup>53</sup>

### Gas Stripping and Vacuum Deaeration

Gas stripping implies that dissolved gases are removed from liquids using pressure reduction, heat, or an inert gas (stripping vapor—usually natural gas). Some processes use all three of these principles.

Most topside corrosion is due to the presence of oxygen. Vacuum deaerators and other thermal-mechanical means are used to remove dissolved gases, to include oxygen, from liquids. These systems can effectively reduce the dissolved oxygen levels to 20–50 ppb. Further oxygen removal is then possible using oxygen scavengers, a form of corrosion inhibitors. Issues with mechanical removal of dissolved gases include the initial capital costs and maintenance. Fouling with solids and bacteria can reduce efficiency, and defoamers may become necessary.<sup>54</sup>

### Corrosion Inhibitors

Corrosion inhibitors are substances which, when added to an environment, decrease the rate of attack by the environment. Removal of oxygen, if present, with oxygen scavengers and adjustment of the pH to levels above 10 usually substantially reduces corrosion rates. While these approaches work in many aqueous environments, they are not practical for many production fluids, and the use of corrosion inhibitors, chemicals added to the environment in small concentrations, will often

become necessary. These corrosion inhibitors will often reduce the corrosion rate to approximately 5–10% of the corrosion rate with no inhibitors.

The use of corrosion inhibitors was the main means of internal corrosion control in oil and gas production until the 1980s, when production from deeper, and consequently hotter, formations led to the increasing use of CRAs for environments where corrosion inhibitors will not work.<sup>55,56</sup>

Corrosion inhibition can be started or changed *in situ* without disrupting a production process. This is a major advantage over other corrosion control techniques, and it also means that the inhibitor chemistry or dosage rate can be changed as a field ages and sours or other conditions alter the corrosivity of the environment.

There are many other chemical treatments used for oilfield production fluids, and corrosion inhibitors must be compatible with them. The most common compatibility problems are associated with hydrate inhibitors. Other chemicals used for scale and paraffin control, antifoaming agents, emulsions breakers, and so on, also affect corrosion inhibitor performance, but they will be discussed only as they relate to corrosion control.

**Types of Inhibitors** Corrosion inhibitors have been classified many ways, but one of the most common is into the following groups, based on how they control corrosion:<sup>57</sup>

- Adsorption or film-forming inhibitors
- Precipitation inhibitors
- Oxidizing or anodic passivation inhibitors
- Cathodic corrosion inhibitors
- Environmental conditioners or scavengers
- Volatile or vapor-phase inhibitors

These groupings and others are shown in Figure 6.58.<sup>58</sup>

Another possible classification is into organic and inorganic inhibitors. Most corrosion inhibitors used for oilfield applications are film-forming organic chemicals, but commercial multicomponent inhibitor packages often contain inorganic oxygen and H<sub>2</sub>S scavengers and oxidizing agents in addition to the film-forming organic components.

Inhibitors do their work at low relative dosages (often expressed in parts per million or quarts per 1000 barrels).

Most oilfield inhibitors work by forming hydrophobic films on metal surfaces. Filming amines, the first of these inhibitors to be widely used in oil and gas production, were developed in the 1940s. Many other organic corrosion inhibitors have been developed since that time. There are a wide variety of commercially available

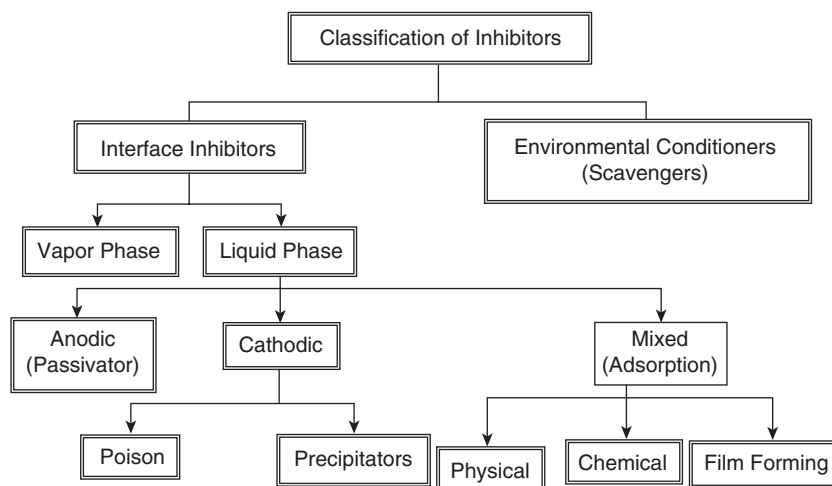


Figure 6.58 Corrosion inhibitor classifications.<sup>58</sup>

proprietary adsorbing inhibitors on the market. They typically have hydrocarbon chains of C12-C18 with amine groups on the hydrophobic end and some other group on the opposite end.<sup>59</sup>

These thin films do not form new compounds on the surface and are considered to be chemisorbed or physisorbed—attached to the surface by relatively weak bonds having less energy than would be associated with chemical compound formation. These inhibitors work because one end of the relatively long-chain organic molecule is attracted to electrically conductive surfaces such as bare metals. The other end of the same molecule is either hydrophobic—it repels water or oleophilic—it attracts oil. This means that the adsorbed inhibitor repels water and avoids water wetting of the metal surface. This is shown schematically in Figure 6.59.

Halides, present in most oilfield waters, tend to increase the efficiency of these inhibitors by increasing adsorption of the slightly positive nitrogen groups present on the hydrophobic ends of these molecules.<sup>57</sup> Oxygen is an enemy of organic inhibitor films, and can both penetrate films and interfere with film formation. For this reason, oxygen is generally removed (or prevented from entering) from oilfield waters that require inhibition with organic adsorbing inhibitors. Most types will not perform well in the presence of more than 0.5 ppm O<sub>2</sub>, or in some cases, as little as a few parts per billion. This is the reason for using them in conjunction with oxygen scavengers in most topside corrosion inhibitor packages and is the reason why effective downhole corrosion inhibition must be supplemented for topside piping and processes, where oxygen entry is more likely.

Adsorbed inhibitor films are very thin and can be removed by mechanical shear forces if the fluid transport past the surface is too fast. The nature of these

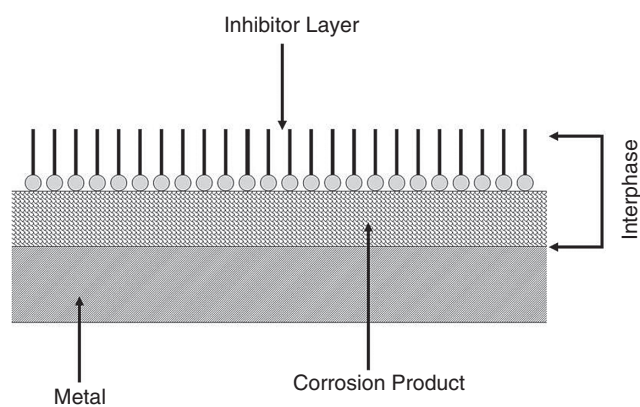


Figure 6.59 Adsorbing corrosion inhibitor with hydrophilic molecular tails away from the metal surface.

filming organic inhibitors is such that they will attach to most solid surfaces, and this means that fluid streams with sand or other solid particles will have reduced inhibitor efficiencies, because the inhibitor will also attach to sand and other particulate matter in the fluid stream.<sup>60</sup> Adsorbed inhibitors will also attach to any scale or corrosion products on the surface, and this also diminishes the corrosion-inhibiting effect.<sup>61</sup> In older systems that have already corroded, it is essential to clean the surface, mechanically or chemically, before applying inhibitors. If rust or mineral scales are present, acid cleaning may be required.

Adsorbed corrosion inhibitors usually cover both anodes and cathodes. Because these inhibitors are based on organic chemicals, they normally cannot be used at elevated temperatures. The upper limit of their use depends on the chemical involved, but 200°C (~400°F) is a common upper limit for the higher-temperature

inhibitors, and most filming inhibitors lose effectiveness at much lower temperatures. These inhibitors, which rely on intimate contact with metallic surfaces, cannot be used in combination with oxidizing inhibitors, which form thick metal oxides on the surface.<sup>57</sup>

There are many proprietary adsorption corrosion inhibitors based on the following base chemistries:

- Amines ( $R-NH_2$ )
- Carboxyls ( $R-COOH$ )
- Thiourea ( $NH_2CSNH_2$ )
- Phosphonates ( $R-PO_3H_2$ )
- Benzonate ( $C_6H_5COO^-$ )
- Antimony trichloride ( $SbCl_3$ )

Precipitating inhibitors are film-forming compounds that form precipitates and cover the metal surface with mineral films that prevent water from reaching the metal surface. Silicates, phosphates, and molybdates fall into this category. They are used in process water and find limited use in oilfield fluids and production streams. Silicate inhibitors have the unusual property of being effective in already-corroded systems where most other corrosion inhibitors lose their effectiveness.<sup>57</sup> Other precipitating inhibitors include calcium salts (calcium carbonate and calcium phosphate) and zinc salts (zinc hydroxide and zinc phosphate). Calcium compounds are widely used in potable water systems to maintain the pH of water at a high level (typically around pH 8–9) and with a slight oversaturation of calcium in the water so that any exposed surfaces will be covered with thin carbonate scales. This has been standard potable water treatment practice since the 1920s.<sup>1,3,58</sup>

Passivating inhibitors that oxidize metal surfaces are commonly used in steam and water systems, but they are seldom used before effective hydrocarbon-water separation has occurred. They also tend to be ineffective in high-chloride waters like the majority of produced water systems.

Chromates are the most effective passivating inhibitors, but environmental concerns have limited their use, especially for any application where water discharge is possible. Alternatives to chromates are not as effective, although research continues on their development. At present, most non-chromate oxidizing inhibitors are based on nitrites, which are considered to have fewer environmental problems than either chromates or phosphates. Bacterial decomposition of nitrites limits their use in open recirculating water systems. Molybdates and tungstates are also available. None of these oxidizers work in the presence of  $H_2S$ .<sup>57</sup>

Indirect passivators are alkaline chemicals that increase pH by reacting with hydrogen ions and remov-

ing them from the surface so that oxygen can adsorb onto the surface and react with the metal. Unlike the direct passivators, these corrosion inhibitors will not work in the absence of dissolved oxygen. Inorganic direct passivators include  $NaOH$ ,  $NaOH$ ,  $Na_3PO_4$ ,  $Na_2HPO_4$ ,  $Na_2SiO_3$ , and  $Na_2B_4O_7$  (borax). Organic indirect passivators include sodium benzoate and sodium cinnamate. These organic passivators have the advantage of not causing pitting corrosion if the chloride ion becomes too concentrated, but the general weight loss corrosion rate does increase.<sup>57</sup>

Most proprietary oxidizing (passivating) inhibitor packages have a combination of several active ingredients.<sup>57</sup>

Oxygen and  $H_2S$  scavengers remove aggressive gases from water and lower corrosion rates. pH control is used to maintain water pH levels at controlled levels—high enough to limit corrosion but low enough to avoid unwanted scale deposits.

Oxygen scavengers do not work in acids and have no effect on pH. For this reason, they are often used in conjunction with some form of pH adjustment, which is also necessary for both corrosion and scale deposition control. Sodium sulfite, ammonium bisulfite, and sulfur dioxide are examples of commercial oxygen scavengers, but others are also available.<sup>53</sup> Nitrites are often used for  $H_2S$  scavenging, which limits corrosion and also inhibits sulfate-reducing bacteria problems.<sup>53</sup>

While oxygen scavengers are often combined with mechanical deaeration for large systems, the use of chemicals alone is sometimes justified for smaller systems.<sup>53</sup>

At one time, the boiler industry used hydrazine ( $N_2H_4$ ) as the primary oxygen scavenger for boiler water feedwater. Hydrazine had several advantages, including the fact that the by-products of its use were nitrogen gas and water. Unfortunately, hydrazine is carcinogenic, and the use of hydrazine has diminished in recent years.

Seawater and other water injection systems frequently use oxygen scavengers to control corrosion and, equally important, to minimize the possibility of microbial fouling of subsurface formations.

Most scavengers used in the oil field are based on sulfites, bisulfites, or nitrites, but they are usually sold as proprietary chemical packages, with minimal identification of their chemistries, as either oxygen or  $H_2S$  scavengers. The  $H_2S$  scavengers will often raise the pH of water and, if calcium carbonate scaling is a potential problem, they must be used in conjunction with scale inhibitors.

Batch processing of scavengers is possible, for example, for drilling fluids, but continuous injection is more common.

Various chemicals are used to neutralize and buffer the pH of liquids. If an acid condenses from a liquid, for

example, gas condensate in wells or pipelines, the neutralizer must condense at the same temperature and pressure. This pH control is often necessary to prevent corrosion at low pHs and to prevent scale deposition, which can also lead to microbial corrosion, at higher pHs.

In boiler water systems, it is common to use morpholine, an organic compound  $O(CH_2CH_2)_2NH$ , at parts per million concentrations for pH adjustment. Morpholine is used for this purpose because its volatility is similar to water, and once it is added to water the morpholine concentration becomes relatively evenly distributed in both the liquid and vapor phases. Hydrazine or ammonia oxygen scavengers are often used in conjunction with morpholine treatment.<sup>57</sup>

It is important to note that oxygen scavengers and oxidizing or passivating treatments work on opposite principles, and the chemicals for these two purposes should not be used concurrently in the same system.<sup>57</sup>

Other environmental conditioning normally involves keeping the pH in an acceptable range. Low pHs promote corrosion and high pHs lead to scaling.

Most vapor-phase corrosion inhibitors are low-molecular-weight amines that condense and form adsorbed films on metal surfaces. While some of these inhibitors have nitrites, which work as oxygen scavengers, most are merely amines. One example would be diethylamine which, when used in sour gas, produces iron sulfide films on the surface which are protective in low-temperature relatively dry gaseous environments.<sup>57</sup>

Most commercial corrosion inhibitor packages are complex blends of many different chemicals, only a portion of which are the nitrogen-containing materials considered to be the primary film-forming chemicals. These other chemicals can be damaging to elastomeric seals and similar polymeric components of the system. NACE has issued a report on this problem, but testing to insure that the problem does not exist is often necessary.<sup>62</sup>

Other compatibility problems are related to the use of hydrate inhibitors and other chemicals added to the system. It is common to test mixtures of these proposed chemicals to determine if one or the other chemical package will interfere with the performance of the other chemicals.

Inhibitor breakdown, for example, at unforeseen elevated temperatures, can also lead to additional corrosion problems.<sup>63</sup>

**Application Methods** Inhibitors are injected continuously (the preferred method) or in batch treatments, which may be necessary for some systems.<sup>65</sup> Most inhibitor injection systems are manufactured from 316L stainless steel, although some lines of PTFE or nylon are used if the pressures and temperatures are low.

Continuous injection is almost universally used except for downhole and pipeline applications where injection sites are difficult to establish and maintain. It is recommended that the corrosion rates be determined upstream of the inhibitor injection location so that the effectiveness of the inhibitor can be determined.<sup>65</sup> Inhibitor injection rates are then adjusted so that acceptable corrosion rates are obtained at the end of the line. If corrosion rates are unacceptably high, then the injection rate can be changed.<sup>64</sup> These changes are likely as a field ages and the corrosivity of produced fluids change.

The initial corrosion inhibitor dosage will usually be very high to satisfy inhibitor demand for the exposed metal and to insure complete filming. Once this initial filming has been accomplished, the dosage rate is dropped to a minimum level necessary to maintain the film under operating conditions.

Corrosion inhibitor batch treatments are used for downhole tubing and for subsea pipelines. They must have low solubility in the system fluids. Batch treatments are characterized by short periods of high inhibitor dosages followed by long periods where the inhibitor level is relatively low. This affects the way these chemicals react with seals and other polymeric materials in the system.<sup>64</sup>

Batch treatments involve a relatively short period of inhibitor feeding followed by a long period on nonfeeding, where one of the following systems operates:

- The inhibitor films is persistent and lasts for a relatively long time.
- A reservoir of inhibitor slowly feeds into the system needing corrosion control.

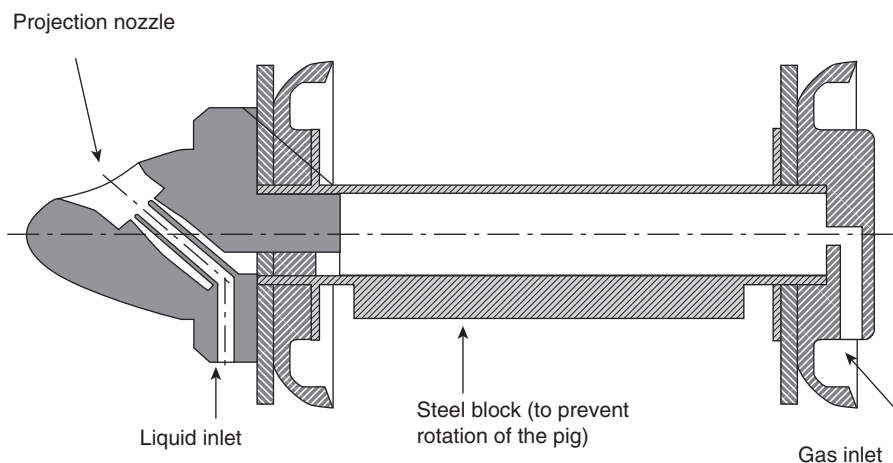
Batch treatments will last from 1 week to several months between treatments.

Tubing displacement batch treatments are used in wells where a batch of corrosion inhibitor is pushed down into the tubing to the bottom of the well. The well is shut in for several hours and then returned to production. This technique is used in wells with packers and with gas-lift wells.

Squeeze treatments are similar to tubing displacements except the inhibitor is displaced beyond the bottom of the tubing and into the geological formation. During this displacement, the system seals are subjected to high concentrations of inhibitor. Once the well is returned to production, the inhibitor concentration slowly lowers as inhibitor is washed from the formation by the produced fluids. Squeeze treatments are usually done monthly or semiannually.

Batch treatments are also common in pipelines, especially subsea pipelines where access is limited. Pigs force inhibitor into the pipeline and this coats the pipe wall.





**Figure 6.60** Venturi pig for spraying corrosion inhibitor onto the top of a pipeline interior to control top-of-the-line corrosion.<sup>66</sup>

This can be done with spiral foam pigs, gel pigs, or special pigs designed to spray inhibitor onto the top of the pipeline interior (Figure 6.60). A typical pig run in a subsea pipeline is intended to provide corrosion inhibitor that will last for a month.

**Testing and Monitoring** Laboratory and field testing are commonly used to determine which of many possible corrosion inhibitor systems should be used in any given application. Testing in the laboratory can reduce the number of inhibitor packages under consideration by quickly eliminating those deemed to be unsuitable. Important parameters to be tested include shear testing—the ability of the inhibitor to “stick” to the metal surface when liquids are moving parallel to the surface at high velocities—which helps determine the inhibitor persistency.<sup>67</sup> Other tests are intended to measure shear testing at higher flow rates, partitioning of inhibitors between water and hydrocarbon phases, and so on.<sup>67–70</sup> It is best if the tests are conducted using the actual fluids from the field, because the presence of minor variables, for example, organic acid contents, in crude oil will affect the ranking of prospective corrosion inhibitors.

While a variety of standardized laboratory tests are available, no consensus exists on their relevance to actual field performance.<sup>71,72</sup> The lack of confirmation of results between different laboratories conducting supposedly comparable tests means that laboratory screening tests cannot be relied upon to produce definitive answers on the best corrosion inhibitors for any given field. This must be determined by field tests.

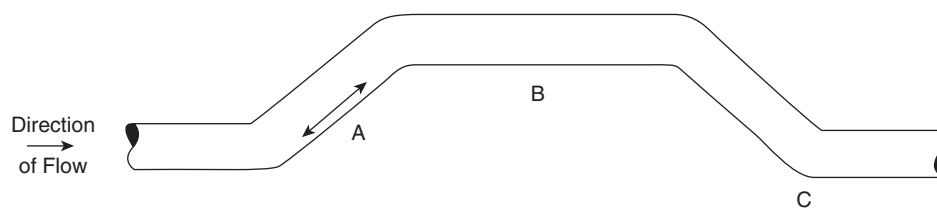
Once preliminary laboratory tests have narrowed the possibilities, prospective inhibitor packages can be com-

pared by field testing. In the past, this has been done by using exposure coupons. Unfortunately, this is a very expensive and time-consuming process. Recent reports indicate that the total time to conduct laboratory and field testing can be substantially reduced using enhanced electrical resistance (ER) probes to produce data on corrosion inhibitor performance in approximately 96 h for each inhibitor tested in contrast to the 36 days previously required. Much of the reduction in time for field testing is due to the introduction of modern, quick-response ER probes that can indicate changes in corrosion rates due to upsets, in a matter of hours instead of days.<sup>73</sup>

It is important to note that all of these tests, both laboratory and field, require the use of replicate samples and testing at various inhibitor dosage levels, for example, steps at 15, 30, and 50 ppm of inhibitor. An inhibitor that works well at one dosage might not be demonstrably better at a higher dosage.

Corrosion inhibitor performance monitoring is necessary to confirm that the corrosion inhibitors and dosage rates that have been selected are appropriate for the field in question. Corrosion coupons pulled every 90 days have become the standard method of insuring that adequate corrosion control has been established. Unfortunately, these coupons cannot identify when in the 90 days most of the corrosion has occurred. ER probes should be used to supplement the coupon data, and it is recommended that two access fittings, one for flush-mounted coupons and one for flush-mounted ER probes should be mounted, normally at the 6 o'clock position, for each monitoring station.<sup>64</sup>

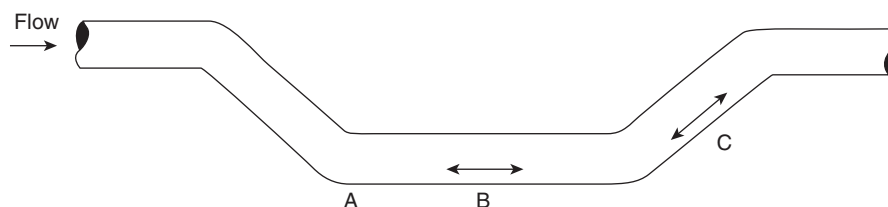
It is very important that coupons be located in locations where maximum corrosion rates can be expected.



a: With Low Flow Rate (Below Limiting Velocity)\*

- A Water oscillates—corrosion accelerated.
  - B Corrosion not accelerated.
  - C Water impinges at C—corrosion accelerated with higher flow rate (above limiting velocity).\*
- Corrosion most severe at impingements.

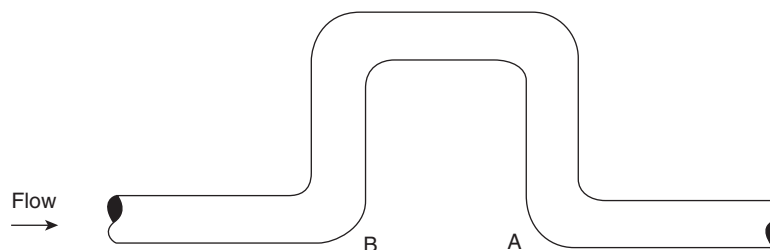
\*Limiting Velocity—velocity above which erosion damage can be expected.



b: Low Flow Rate

Corrosion most severe at B and C.

High Flow Rates  
Corrosion most severe at A.



c: Vertical Riser in Gas Line Carrying Small Volume of Water

- A In high-velocity flow, water impinges on Points A and B, accelerating corrosion.
- B At low velocity, water accumulates in upstream leg of loop, cascades down in downstream loop, impinging at Point A.

**Figure 6.61** Locations for coupon installation in a wet gas piping system.<sup>74</sup>

Suggested locations for coupon locations along a wet gas piping system are shown in Figure 6.61. The ideas represented in this figure should be considered in placing corrosion coupons, ER probes, and other monitoring devices—they should be placed at locations where water accumulation and accelerated corrosion are most likely. For gas pipelines, the possibility of top-of-the-line corrosion must also be considered.

Unfortunately, the exact locations where corrosion rates are likely to be the highest are hard to predict. The most aggressive locations will change, especially for multiphase systems, as temperatures and pressures change and fields age, altering the composition and production rates of produced fluids. Monitoring with coupons and ER probes is no substitute for inspection—the two techniques are complementary, and one cannot

substitute for the other. NACE provides suggestions on the corrosion rates to be expected, as shown in Table 6.13.<sup>74</sup>

Unfortunately, too many organizations spend so much time collecting coupons and reporting weight loss data, that they forget to question whether the data have been collected at the correct locations and what it means. Organizations with thousands of coupons showing that corrosion is under control have still had unfortunate leaks due to corrosion at locations where corrosion could have been predicted and inspections could have identified the problems. This is especially true as fields age and production rates decline, leading to more corrosive conditions, especially at locations like those shown in Figure 6.61. The practice of having the same organization that applies corrosion inhibitors also conduct monitoring on the effectiveness of the inhibitor program can lead to unnecessary difficulties.

**TABLE 6.13 Qualitative Characterization of Carbon Steel Corrosion Rates for Oil Production Systems<sup>75</sup>**

	Average Corrosion Rate		Maximum Pitting Rate	
	mm/y <sup>a</sup>	mpy <sup>b</sup>	mm/y	mpy
Low	<0.025	<1.0	<0.13	<5.0
Moderate	0.025–0.12	1.0–4.9	0.13–0.20	5.0–7.9
High	0.13–0.25	5.0–10	0.21–0.38	8.0–15
Severe	>0.25	>10	>0.38	>15

<sup>a</sup> mm/y, millimeters per year.

<sup>b</sup> mpy, mils per year.

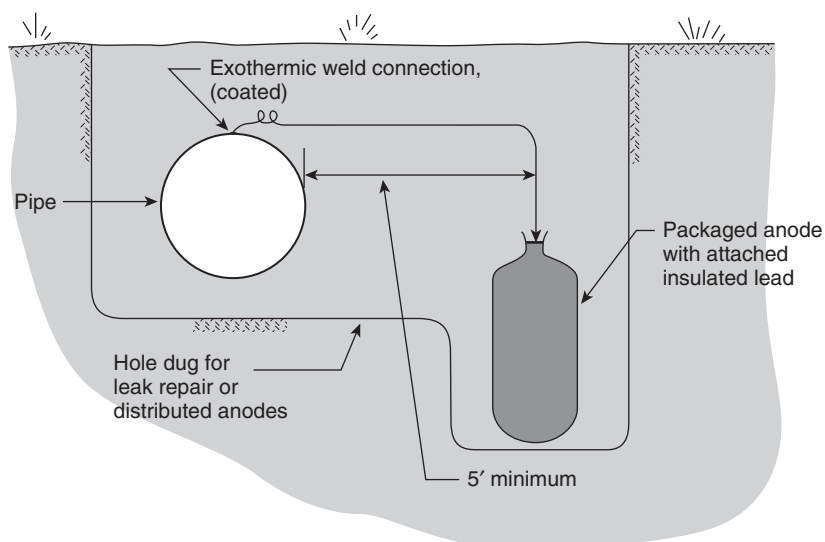
## CATHODIC PROTECTION

Cathodic protection is an electrical means of corrosion control where the structure to be protected is made the cathode in an electrochemical cell. Oxidation of the electrochemical cell is shifted to anodes leaving the structure to be protected as a cathode with a net reduction reaction which suppresses the corrosion rate. While many oilfield structures are cathodically protected, this discussion will emphasize pipelines, the most common cathodically protected structures in oil and gas production. The principles discussed here for pipelines apply to any cathodically protected structure.

Figure 6.62 shows a simple cathodic protection system for a buried pipeline. The pipeline is connected by a lead wire to a buried magnesium anode which corrodes at an accelerated rate thereby providing protective cathodic current to the pipeline.

The combination of protective coatings as the primary means of corrosion control and cathodic protection as a supplemental secondary means of corrosion has proven most economical for most pipelines and similarly buried or submerged structures. The electrical current demands of the cathodic protection system are determined by the effectiveness of the protective coating, and they increase as the protective coating ages and degrades.

Cathodic protection allows carbon steel structures, which have limited natural corrosion resistance in many oilfield environments, to perform with little or no corrosion, provided the cathodic protection system is designed, installed, and maintained correctly. It was discovered in the nineteenth century and used on British



**Figure 6.62** A single packaged anode buried in soil to protect a buried pipeline.<sup>76</sup>

naval vessels. Its use on pipelines dates to the early 1900s work of R. Kuhn and coworkers, who used cathodic protection to lower the corrosion rates of buried onshore pipelines in Louisiana.<sup>76,77</sup>

The corrosion (oxidation) reaction on a buried steel structure is:



The buried anode undergoes a similar reaction:



Reduction reactions depend on the pH of the water in the environment, but are usually:

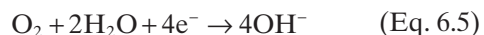
In acids:



Or



In neutral or basic solutions:



Except in strong acids ( $\text{pH} < \sim 3$ ), the concentration of oxygen is most likely to predominate, and most of the reduction reaction on a cathode will be oxygen reduction.

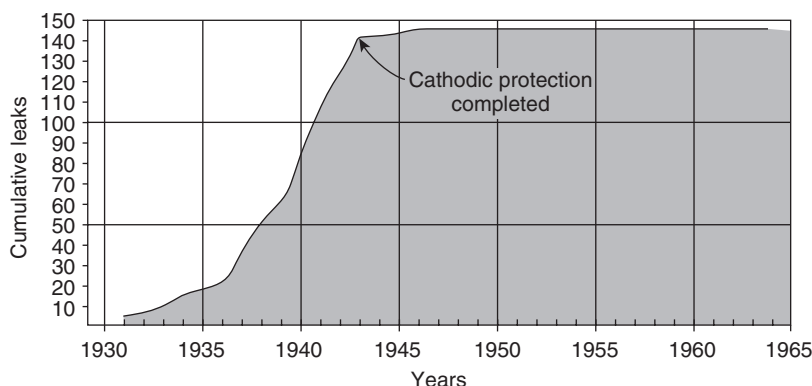
In order for cathodic protection to work all components of an electrochemical cell, anode, cathode, electrolyte, and return circuit must be present. The absence of any one of these will prevent successful cathodic protection. Sometimes people forget this, for example, with attempts to protect high-temperature pipelines where the environment is so hot that water evaporates and no electrolyte is present to transmit electric current.

## How Cathodic Protection Works

The effectiveness of cathodic protection can be expressed in many ways. The first arguments for its use on pipelines and other oilfield structures emphasized the reduction in leaks due to external corrosion. This type of data was used by R. Kuhn, who presented data in the 1930s showing a major reduction in leaks on natural gas pipelines due to the use of cathodic protection.<sup>76-79</sup> While cathodic protection had been described in the 1800s and used to protect nails holding copper sheathing to the bottom of British ship hulls, Mr. Kuhn is generally recognized as the first engineer to use cathodic protection in the United States, where he applied it to controlling corrosion of cast iron natural gas pipelines starting in 1913.<sup>79</sup>

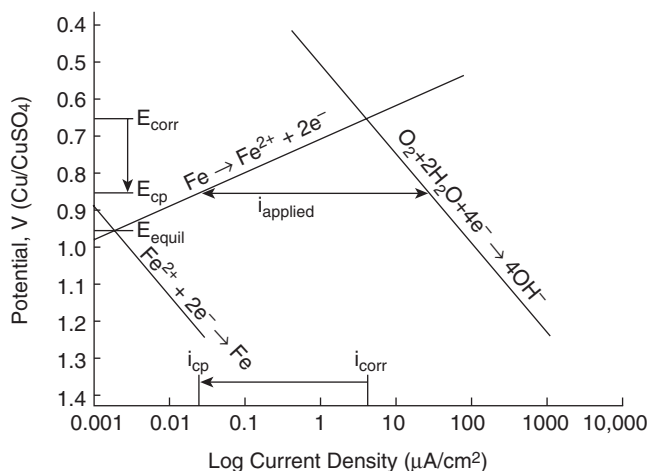
Figure 6.63 shows the reduction in leaks on a major pipeline system due to the application of cathodic protection.<sup>80</sup> This figure shows data from the 1940s and later, when the idea of cathodic protection started to gain widespread attention along the Gulf Coast of the United States. Discussions among Gulf Coast pipeline operators led to the formation in 1945 of the organization that has become NACE International, the largest organization devoted to corrosion control.<sup>79</sup>

The Evans diagrams (potential vs. log current) in Figures 6.64 and 6.65 illustrate the principles of cathodic protection. The corrosion (oxidation) reaction is shown by the line which goes up and to the right in Figure 6.64. The intersection of this oxidation reaction with the reduction reaction for dissolved oxygen in the electrolyte determines the corrosion rate. In Figure 6.64, the corrosion rate is reduced by over two orders of magnitude by the application of cathodic protection. Note that the potential of the cathodically protected iron, shown at  $-0.85\text{V}$  ( $\text{Cu}/\text{CuSO}_4$ ), is above the equilibrium potential and that the corrosion rate, while reduced by more than two orders of magnitude, is not zero.



**Figure 6.63** Effectiveness of cathodic protection in stopping the development of pipeline leaks.<sup>80</sup>





**Figure 6.64** Evans diagram showing the principles of cathodic protection.<sup>81</sup>

Figure 6.64 is used in a standard reference work on pipeline corrosion to explain how cathodic protection works. The same idea has been published previously.<sup>79</sup> It is deliberately simplistic and slightly unrealistic, because the corrosion rate of most buried or submerged steel is controlled by the diffusion of oxygen to the metal surface and not by hydrogen ion reduction. This means that the reduction reaction, shown as a slanting straight line in Figure 6.64, is more likely to be a vertical line indicating that the reaction is under oxygen diffusion control (concentration polarization) as shown in Figure 6.65.

Both figures make the same points:

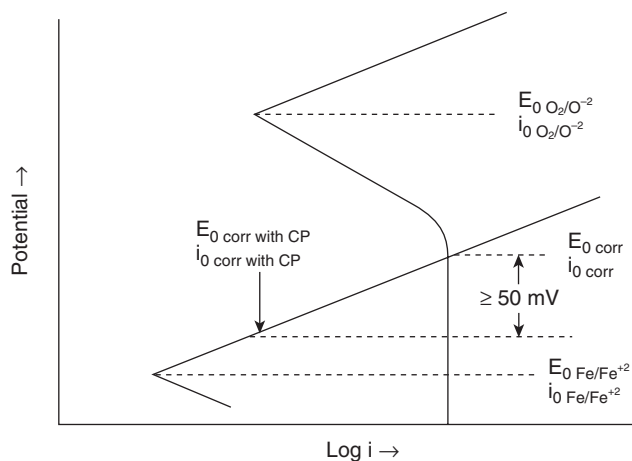
- Cathodic protection substantially reduces the oxidation current (corrosion) of the structure being protected.
- Cathodic protection does not stop corrosion—it reduces the corrosion rate, hopefully to a negligible, or at least an acceptable, rate.

Note that neither diagram suggests that the potential after cathodic protection is below the equilibrium potential where the current for oxidation of iron is equaled by the current for reduction of iron ions.

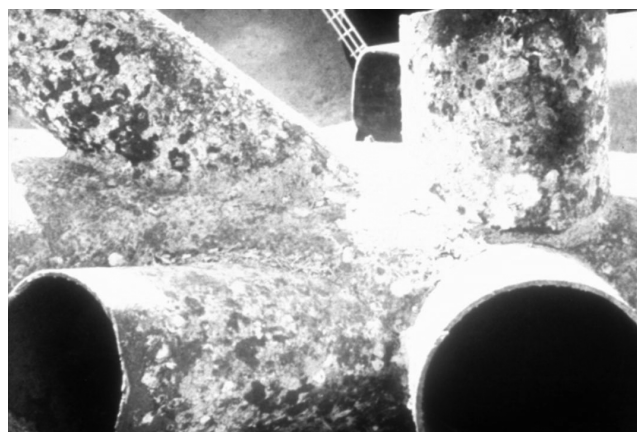
While Evans diagrams, like those shown above, are used to explain cathodic protection, they were not used by the people who developed these techniques in the early-mid-twentieth century.

In the oil field, cathodic protection is applied to pipelines in soil and water environments, to offshore structures, and to process and storage vessels.

Cathodic protection is usually used in conjunction with protective organic coatings. The protective coating is considered the primary means of corrosion control,



**Figure 6.65** Evans diagram showing cathodic protection with the reduction reaction limited by oxygen diffusion control.



**Figure 6.66** Calcareous deposits formed by cathodic protection on an offshore platform node. Photo courtesy of J. Smart.

and the cathodic protection system is sized to provide corrosion control at defects in the coating. As the coating ages and becomes less protective, the demands for electrical current from the cathodic protection system increase. This combination of protective coatings and cathodic protection has become standard on most oil-field equipment. The exceptions are most offshore structures and some process equipment, which are often used in the uncoated state. Cathodic protection causes a pH shift, shown in Equations 6.3 through 6.5, to higher pHs, where most minerals are less soluble. The pH shift produces precipitates of calcareous deposits, usually calcite but sometimes other minerals, on the protected surface. These mineral deposits reduce the exposed metal surface and act as protective coatings on offshore structures.<sup>82,83</sup> Figure 6.66 shows calcareous deposits caused by cathodic protection on the node of an offshore plat-

form in a warm shallow sea. Whitish deposits cover most of the surface, but even the darker areas are covered with scale so hard that it is difficult to remove it with a hammer and chisel.

The oxidation at anodes in cathodic protection systems alters the potential of the protected structure and shifts it in a cathodic direction. While several reduction reactions are possible on cathodically protected surfaces, the most common reaction is the reduction of dissolved oxygen or, if the pH is low or the negative potential is large, the evolution of hydrogen gas.

Note the logarithmic slope of the oxidation (corrosion) rates in Figures 6.64 and 6.65. Neither of these figures implied the total elimination of corrosion. Small shifts of potential produce drastic reductions in corrosion rates, and it has been reported that a cathodic potential shift of  $-70\text{ mV}$  to  $-100\text{ mV}$  will reduce the corrosion rate to 10% of the original corrosion rate.<sup>84</sup> Cathodic protection *reduces* but does not eliminate corrosion. “A major activity of a CP engineer is to determine the actual level of CP required to reduce the corrosion rate to an acceptable level.”<sup>81</sup>

### Types of Cathodic Protection

There are two types of cathodic protection, galvanic-, or sacrificial-anode, cathodic protection and impressed current cathodic protection (ICCP).

**Galvanic Anode Cathodic Protection** Figure 6.61 showed a simple galvanic cell using a buried magnesium anode to protect a buried steel pipeline. Table 6.14

**TABLE 6.14 Galvanic Series of Metals in Soil**<sup>85</sup>

Material	Potential (volts CSE) <sup>a</sup>
Carbon, graphite, coke	+0.3
Platinum	0 to $-0.1$
Mill scale on steel	$-0.2$
High-silicon cast iron	$-0.2$
Copper, brass, bronze	$-0.2$
Mild steel in concrete	$-0.2$
Lead	$-0.5$
Cast iron (not graphitized)	$-0.5$
Mild steel (rusty)	$-0.2$ to $-0.5$
Mild steel (clean and shiny)	$-0.5$ to $-0.8$
Commercially pure aluminum	$-0.8$
Aluminum alloy (5% zinc)	$-1.05$
Zinc	$-1.1$
Magnesium alloy (6% Al, 3% Zn, 0.15% Mn)	$-1.6$
Commercially pure magnesium	$-1.75$

<sup>a</sup> Typical potential normally observed in neutral soils and water, measured with respect to copper sulfate reference electrode.

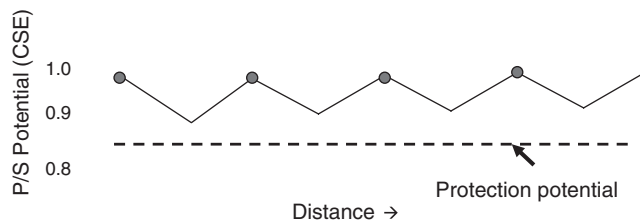
shows the potentials of selected metals in soil. Carbon steel and cast iron are naturally cathodic to most other structural metals. They are, however, cathodic to magnesium, aluminum, and zinc—the metals used for galvanic anodes.

Figure 6.61 showed a simple single anode attached to a pipeline. The anode, which corrodes to protect the structure, is located at a “remote” location, as far away from the pipeline as is practical. The purpose of this remote location is to insure that the current from the anode is distributed to “ground,” so that current is not wasted near the anode–wire–lead connection location. Current then comes from “ground” to the holidays in the protective coating on the pipeline instead of being concentrated near the anode–wire–lead connection to the pipeline.

Galvanic anodes are typically supplied with approximately 3–5 m (10–15 ft) of lead wire, which is sufficient to locate the anodes at “remote earth” in most environments.

Galvanic anodes are often installed in “distributed anode” configurations. One anode protects a given length of pipe and, where the IR drop down the pipeline is too much and inadequate protection is available, another anode is located. The critical location is midway between the two anodes. This is shown in Figure 6.66. Note that the potential varies from approximately 1 V to somewhat more than 0.85 V. Since all voltages are negative relative to copper/copper sulfate electrodes, the potentials are plotted with larger negative numbers on top. This is in accordance with convention for cathodic protection, but seems backward compared to conventional engineering practice. As long as the potential remains more negative than the protection potential (above the dotted line in Figure 6.67), corrosion on the pipeline will be minimized and the structure will be cathodically protected.

The potential profile in Figure 6.67 shows that the pipeline is more protected than necessary near the anodes and that the potential decays as the distance from the anode increases. The spacing between anodes is determined by the IR drop down the pipeline and by



**Figure 6.67** Potential plot along a pipeline with galvanic anode cathodic protection.

the current demand on the pipeline exterior. A typical spacing between anodes is of the order of hundreds of meters (yards), but there are wide variations depending on protective coating quality, diameter of the pipeline, and corrosivity of the environment.

Because the voltage of galvanic anodes is limited, the spacing between anodes is often the design-limiting parameter. This leads to increased construction costs on long-distance pipelines, and galvanic anodes are seldom used onshore for long-distance pipelines. They are used on small structures, in low-resistivity environments—where they can be relied upon to work, and for protecting “hot spots” where corrosion is intensified.<sup>80</sup>

Table 6.15 lists some advantages and limitations of galvanic anode systems. The typical design life of onshore galvanic anodes is 5–10 years, although some anodes perform for much longer. Potential surveys, described below, are necessary to determine when the anodes have neared or reached the end of their useful life.

Three different metals are commonly used for galvanic anodes—magnesium, zinc, and aluminum. Carbon steel is sometimes used for cathodic protection on process equipment fabricated with CRAs, but carbon steel anodes are not commercially available from most suppliers. Table 6.16 shows typical applications for each of the common galvanic anode metals.

While it is common to refer to these materials by their primary constituent, all these anode materials are

alloyed to insure that they will reliably corrode and produce the necessary current for cathodic protection.

There are two commonly used magnesium anode alloys. The high-potential alloys have a native potential in soil of approximately  $-1.80\text{V}$  relative to copper/copper sulfate, and the H1 or AZ-63 anodes have a potential of  $-1.55\text{V}$ . Table 6.17 lists important properties of these alloys.<sup>86</sup>

Most of the cost of galvanic anode installation is labor and excavation. Thus, the onshore installation costs for galvanic anodes are essentially the same for all anode sizes. The 17-lb (7.7kg) anode is the most commonly used size in North America.

Most applications use the high-potential magnesium-manganese alloy developed by Dow Chemical Company in the 1950s.<sup>86</sup>

Quality control problems with magnesium anodes have occurred in recent years, and many anode suppliers have been forced to conduct quality control testing on magnesium anodes.<sup>86,87</sup>

Anode efficiency for magnesium anodes is 50% under normal conditions. This means that half of the electrical current produced by the corrosion of the anodes will be available for cathodic protection. The efficiency is less at low pHs.

Magnesium anodes are the most reliable of all galvanic anode materials—they will corrode in almost any wet environment. Nonetheless, they are normally

**TABLE 6.15 Advantages and Limitations of Galvanic Anode Cathode Protection Systems**

Advantages and Limitations of Galvanic Anode Cathodic Protection Systems	
Advantages	Limitations
No external power required	Limited driving potential
Easy to install	Lower/limited current output per anode
Simple—can be installed and maintained with minimally trained personnel	May not work in high-resistivity environments
Minimum maintenance	High cost per ampere year of current generated
Installation can be inexpensive if installed during construction	Installation can be expensive on long pipelines—requires many installations
Relatively uniform distribution of current	
Not a source of stray current	
Cannot be turned off—always active until anodes consumed	

**TABLE 6.16 Primary Uses of Galvanic Anodes in Oilfield Applications**

Magnesium
Onshore buried structures
Process equipment
Zinc
Marine pipelines
Process equipment
Freshwater ballast tanks
Ship hulls
Aluminum
Offshore structures
Limited use in process equipment

**TABLE 6.17 Electrochemical Properties of Magnesium<sup>86</sup>**

A-h/lb theoretical	1000
Current efficiency (based on $\sim 30\text{mA}/\text{ft}^2$ )	50%
A-h/lb actual	500
Consumption rate, lb-A-yr	17.4
OCP	V to Cu/CuSO <sub>4</sub>
AZ-63 (H-1) alloy	$-1.50$ to $-1.55\text{V}$
High-potential alloy	$-1.75$ to $-1.77\text{V}$

supplied with prepackaged backfills. The most common magnesium anode, 17lb (7.7kg), will weigh about 45lb (20kg) when the weight of the prepackaged backfill is added. This backfill is intended to provide a low resistivity and wet environment to the anode. Most backfills are a combination of a hygroscopic soil (gypsum and/or bentonite clay) and ionic salts (calcium chloride).

Zinc anodes were used as early as 1824 to protect the nails holding copper cladding to the bottom of wooden ships. Alloy additions of aluminum and cadmium increase the efficiency of modern zinc anodes and also produce more uniform corrosion.

The potential of zinc in most soils is assumed to be  $-1.1\text{V CSE}$ . This voltage is much lower than that for magnesium, but the efficiency of zinc anodes is generally considered to be  $\sim 90\%$ , so much more of the electricity generated by corrosion of the anode is available for cathodic protection.

Unlike magnesium, zinc will not corrode in many soils, and the use of zinc in soils has been restricted to low-resistivity soils ( $<1000$  to  $2000\ \Omega\text{-cm}$  depending on the authority in question).<sup>88</sup> Recent quality control problems with magnesium anodes have caused many organizations to use zinc anodes onshore in applications where they would not have been considered in previous years. Proponents of the use of zinc anodes for pipeline cathodic protection argue that both zinc and magnesium can produce adequate current to polarize pipelines having the high-quality coatings that have been introduced in recent years. Magnesium is alleged to corrode too fast, wasting electricity, whereas zinc will provide enough current and last longer.<sup>88</sup> The same type of prepackaged backfills that are used for magnesium are supplied for zinc anodes. The backfills produce wet soil environments having resistivities in the hundreds of  $\Omega\text{-cm}$  (ohm-cm). This low-resistance environment should corrode both zinc and magnesium. This practice of substituting zinc for magnesium is controversial and should only be used with careful monitoring to insure that the desired cathodic protection is achieved. Many operating companies continue to avoid the use of zinc anodes except in soils with naturally low resistivity (usually high moisture swampy or coastal soils).

Table 6.18 summarizes the characteristics of zinc anodes.

Temperatures above  $60^\circ\text{C}$  ( $140^\circ\text{F}$ ) have been found to cause zinc to be cathodic to carbon steel in some freshwater environments. This should not be a problem in seawater and other high-chloride environments.<sup>1</sup>

For marine applications, zinc anodes, which last longer than magnesium, are less efficient than aluminum anodes. Zinc should only be used in brackish water when the chloride concentration falls below approximately 6–10ppt (parts per thousand) compared to

**TABLE 6.18 Zinc Anode Characteristics**

Element	Mil Spec	ASTM B-418-01	
	A-18001K	Type I	Type II
Al	0.10–0.50%	0.10–0.50%	0.005% max
Cd	0.025–0.07%	0.025–0.07%	0.003% max
Fe	0.005% max	0.005% max	0.0014% max
Pb	0.006% max	0.006% max	0.003% max
Cu	0.005% max	0.005% max	0.002% max
Si	0.0125% max		
Zn	remainder	remainder	remainder
Use	seawater and brackish water ( $T < 50^\circ\text{C}$ ) [ $120^\circ\text{F}$ ]		soil and freshwater
Nominal potential	$-1.10\text{V CSE}$		
Efficiency	90%		
Capacity	738A-h/kg (335A-h/lb)		
Consumption	11.9kg/A-yr (26.2lb/A-yr)		

approximately 35ppt for open seawater.<sup>89</sup> Under these conditions, aluminum may not corrode and produce the necessary current.

Aluminum anodes have become the standard galvanic anode material for use in offshore applications. Early aluminum anode alloys used mercury as an “activator,” but environmental concerns have caused these mercury-activated anodes to be replaced with indium-activated anodes. Table 6.19 shows the two types of aluminum anodes most commonly used offshore. These anodes cannot be used in freshwater applications, because they will passivate and become inactive if the salt content (commonly expressed as chloride concentration) is too low. This is also the reason why aluminum anodes are not used on ships—they passivate in harbors and will not work once they are back in the ocean. Aluminum anodes can also be used in oilfield process equipment where produced water has a high salt content. Special alloying modifications are also available from some suppliers for use in cold water.<sup>90</sup>

There have been isolated cases where aluminum did not work offshore. These instances have been traced back to freshwater flushing from rivers into the ocean. This has happened as far as 150km (100mi) offshore in the Gulf of Mexico due to the freshwater flow from the Mississippi River. Freshwater is less dense than saltwater, so the tops of the water column near rivers may be fresh while the deeper locations ( $>30\text{m}$  or 100ft) may be salty enough for efficient use of aluminum anodes.

Aluminum anodes for offshore platforms are available in sizes up to 500kg (1200lb) and larger.

Most of them are cast with a steel core which can be welded to the platform leg or other structure.



**TABLE 6.19 Aluminum Anodes for Offshore Use**

Chemical Composition		
Element	Mercury Activated	Indium Activated
Zn	0.03–0.50	2.8–3.5
Si	0.14–0.21	0.08–0.2
Hg	0.035–0.048	—
In	—	0.01–0.02
Cu	<0.01	<0.01
Fe	<0.12	<0.12
Other each	<0.02	<0.02
Al	Remainder	Remainder
Electrochemical Properties		
Use	Open Seawater	Seawater/mud
Potential (Cu/ CuSO <sub>4</sub> )	–1.05	–1.15
Nominal efficiency	95%	85%
Nominal amp hours/pound	1280	1150
Capacity— seawater	2830 A-h/kg 1280 A-h/lb	2530 A-h/kg 1150 A-h/lb
Consumption— seawater	3.10 kg/A-yr 6.83 lb/A-yr	3.48 kg/A-yr 7.83 lb/A-yr
Capacity—mud	—	2180 A-h/kg 990 A-h/lb
Consumption— mud	—	4.02 kg/A-yr 8.87 lb/A-yr

Carbon steel anodes are occasionally used for cathodic protection of CRAs in process equipment—heat exchangers with CRA tubing and protective-coated carbon steel headers and water boxes. Carbon steel galvanic anodes are used to increase the area ratio of exposed carbon steel and lower the corrosion rates of the structural members. This is a relatively unusual application, and most anode suppliers do not carry carbon steel or iron anodes.

Magnesium works in any soil, but high currents during the early years of the system may limit total life and require early replacement. There have been market-driven quality control problems in recent years that have caused some users to substitute zinc anodes with prepackaged backfills. Magnesium has also been used for initial high-current “kick” to build up calcareous deposits early in the life of offshore platforms.

Zinc should only be used on-shore in low-resistivity soils. While the recommended upper limit of acceptable resistivity varies with experts and locations, 1500  $\Omega$ -cm is a common maximum.<sup>88</sup> The use of zinc in combination with low-resistivity prepackaged backfills is relatively

new, and many experts question this approach. Zinc is also used for bracelet anodes on marine pipelines and on ships and smaller vessels.

Aluminum is used offshore on platforms, risers, and pipelines, although zinc bracelet anodes are more common due to concerns that aluminum may passivate in mud.

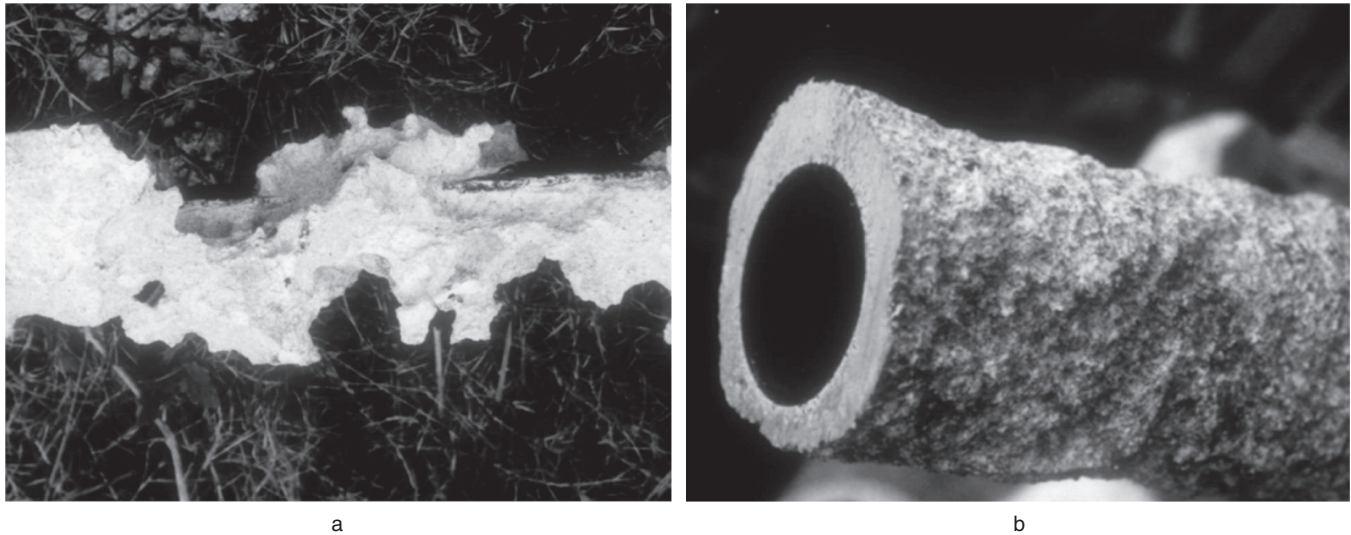
All of the anode materials are used in process equipment, depending on the application and the conductivity of the environment.

Backfill materials are commonly used to guarantee that galvanic anodes will corrode and provide the necessary current to protect the structure. These are usually supplied in water-permeable cloth bags with enough prepackaged backfill soil to more than double the weight of the metal anode. Most galvanic anode backfills contain gypsum, bentonite clay, and an ionic salt such as calcium chloride or sodium sulfate. The minerals in the backfill are hygroscopic and absorb moisture if it is available. They are also ionic and have low resistivity to insure that the backfill will be corrosive whenever wetted. Anodes are sold with prepackaged backfills in cloth bags. Backfill is also sold in 50 lb (23 kg) bags for use with anodes shipped without backfill.

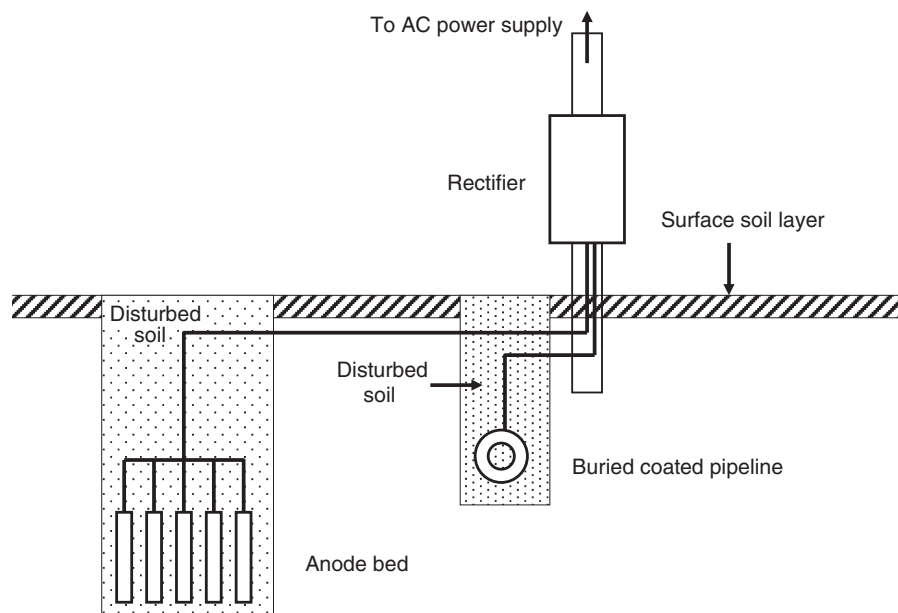
Prepackaged anodes are shipped with plastic wrapping to prevent them from becoming moist and corroding prior to installation. It is unfortunate that many prepackaged anodes are installed with this plastic intact, because the installation crews do not understand the purpose of the various plastic and cloth wraps.

Recent problems with the quality of magnesium anodes have caused many suppliers to institute quality control programs to insure that the anodes will perform as expected.<sup>86,87</sup> NACE International and other organizations provide guidance on quality control test procedures.<sup>86–93</sup> Many organizations develop lists of quality-approved vendors, but this has not always worked, as different sources of anode materials come on the market and shortages in supplies from traditional vendors develop. Figure 6.68a shows the results of improper and proper foundry practice on the corrosion of aluminum anodes.<sup>82</sup> Similar patterns have been reported on other alloy systems.

**ICCP** When large currents are needed or high electrolyte resistivity prevents the use of galvanic anodes, the protective current for cathodic protection is supplied by an ICCP system similar to the one shown in Figure 6.68 for a buried coated pipeline. The cathodic connection to the pipeline is identical to that shown in Figure 6.62 for galvanic anode cathodic protection. The buried pipeline and the anodes are both connected to an electrical rectifier, which converts alternating current to direct current, and imposes cathodic poten-



**Figure 6.68** Corrosion of aluminum anodes: (a) Uneven corrosion of aluminum anode due to improper foundry procedures leading to segregation of alloying elements. (b) Uniform corrosion of aluminum anode as the result of proper foundry practice.<sup>83</sup>



**Figure 6.69** Impressed current cathodic protection of a buried pipeline.

tials on the structure and anodic potentials on the anode bed.

Unlike galvanic anodes, impressed current anodes need not be naturally anodic to carbon steel, and they usually are not. Most impressed current anodes are made from nonconsumable anode materials that are naturally cathodic to steel. The anodes are intended to serve as sites for oxidation of a component of the environment, usually oxygen dissolved in water, and are not

intended to oxidize. Even though they are intended to be nonconsumable, these anodes do degrade with time. Because they are naturally cathodic to steel, they would accelerate corrosion if they were directly connected to the structure they are intended to protect.

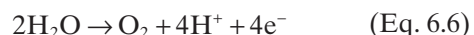
Figure 6.69 shows a typical ICCP system for a buried coated pipeline. The connection to the pipeline is identical to that shown in Figure 6.62 for galvanic anode cathodic protection. The buried pipeline and the anodes

are both connected to an electrical rectifier, which supplies direct current (DC) to both. Unlike galvanic anodes, impressed current anodes need not be naturally anodic to carbon steel, and they usually are not. Most impressed current anodes are made from semi-inert materials that are naturally cathodic (electropositive) to steel. They are intended to serve as electrodes for the transfer of DC current to the environment via an oxidation reaction, which in neutral pH waters and soils produces oxygen. It is intended that these anodes have a relatively low consumption rate. Because they are naturally cathodic to steel, they would accelerate corrosion if they were directly connected to the structure they are intended to protect.

It is important to always attach the leads from the rectifier to the proper terminals. The anode ground-bed leads should always be attached to the positive terminal of the power supply. The negative terminal is always connected to the structure to be protected. Confusion on this point can result in ICCP systems being connected improperly. This causes increased corrosion on the structure rather than the intended reduction in corrosion rates.

The most common oxidation reactions on impressed current anodes are oxidation of dissolved oxygen in the water by one of the two following reactions.

In acids:



In neutral or basic solutions:



Note that the above two reactions are merely the reverse of Equations 6.4 and 6.5, the most common reduction reactions on a cathodically protected surface. All oxidation reactions lower the pH (acidify) of the environment, so Equation 6.6 is the more likely oxidation reaction.

If any chloride ions are in the water, then chlorine evolution can also happen:



All of these reactions produce strong oxidizers which can bleach or oxidize any organic materials nearby. The degradation of early impressed current anode lead wire insulation was once a problem, but modern lead wire insulation is much more resistant to this oxidation. Chlorine gas is also poisonous and care must be taken to vent this gas properly in cases of chlorine evolution.

The anodes used in ICCP are intended to be nonconsumable, but oxidation of these materials does occur to

a limited extent, and care must be taken to operate these anodes at recommended voltages and current densities to prevent premature degradation.

The wiring and connections of the ICCP system must totally isolate the system from the environment. Any exposed metal becomes part of the ICCP circuit and can lead to premature system failure.

Most ICCP uses electric current from a local power source connected through a rectifier, which changes alternating current (AC) to direct current (DC). In locations where conventional electric power is not available, solar cells, batteries, thermoelectric generators, and other DC power sources have been used. At one time, windmills were used in isolated locations, but the maintenance requirements on these mechanical systems have caused them to be replaced in most locations by solar cells.<sup>94</sup>

Figure 6.70 shows a typical cathodic protection rectifier. Most rectifiers will have lead wire connections to the anode bed and to the protected structure as well as connections to an AC power source plus controls and displays to indicate power output, voltages, and current. They will also have lightning arrest capabilities and other safety features and be mounted in protective casings to protect them from the weather, wildlife, and vandalism. All of this costs money, and a typical rectifier, plus installation costs, will run into the thousands of dollars. For these reasons, ICCP is normally limited to situations where large amounts of current are needed, otherwise galvanic anodes would be cheaper.

Most of the cost of rectifier installation is for labor and installation; therefore, it is common to use rectifiers somewhat larger than the measured or calculated



**Figure 6.70** A typical cathodic protection rectifier used for onshore cathodic protection. Photo courtesy of NACE International Basic Corrosion course.

current requirements for the installation would dictate. It is much cheaper to regulate the output of a rectifier than it is to reinstall a larger rectifier if the current demands cannot be met by the existing system. The total cost of installation also leads to the common use of an “anode bed” (also called a “ground bed”) for ICCP systems. While ICCP anodes are intended to be nonconsumable, they have current density limitations. Anode beds with dozens, even hundreds, of anodes are not unusual. The purpose of these large anode beds is to allow for the use of higher-current-output rectifiers, which minimizes the cost of cathodic protection by allowing one rectifier to supply cathodic protection current to large cathode surface areas. It is common for one rectifier/ground bed to provide cathodic protection for several miles or kilometers of buried pipeline. Galvanic anodes, which would need to be placed at hundreds of meters/yards intervals, would be much more expensive for this kind of application.

A typical ICCP system for a pipeline would include an AC powered rectifier with a maximum rated DC output of between 10 and 50 amps and 50V.

There are a number of anode materials used worldwide for ICCP. In relative order of importance they are:

- High-silicon cast iron
- Graphite
- Mixed-metal oxide (MMO)
- Precious-metal clad (platinum)
- Polymer
- Scrap steel
- Lead alloy

The above anodes are sometimes classified into massive anodes:

- High-silicon cast iron
- Graphite
- Scrap steel
- Lead alloy

and dimensionally stable anodes, which tend to be much smaller and less robust:

- MMO
- Precious metal
- Polymer

Each of these materials is discussed in separate sections below.

With the exception of scrap steel, the materials used for ICCP anodes are naturally cathodic to carbon steel

and would accelerate the corrosion of steel structures if they were connected directly to the structure. The purpose of the anodes in ICCP is to serve as a surface for the oxidation of either oxygen or chlorine gases, the two intended reaction products at the anode surface.

High-silicon cast iron anodes for cathodic protection became popular in the 1950s and are still the most commonly used impressed current anode materials. The Duriron Corporation in Dayton, Ohio, developed and marketed the first widely accepted anodes of this type, and they also developed a more corrosion-resistant anode with chromium additions in the 1970s. The patents on these alloys have expired, and both of these alloys are available worldwide. The original grade, ASTM A518 Grade 1 is still specified for some environments, but the more corrosion-resistant alloy, ASTM A518 Grade 3 with chromium additions, is usually specified, because it is more widely available and is more corrosion resistant.<sup>93,95</sup> The most common shapes for these anodes are cylindrical tubes or solid rods up to 210 cm (8 ft) long and weighing up to 127 kg (280 lb).

Buried applications of these anodes usually include a carbonaceous backfill (coke breeze), which increases efficiency by shifting most of the oxidation reaction to the backfill. This backfill prolongs anode life.<sup>96</sup>

Table 6.20 compares the properties of high-silicon cast iron anodes with those of graphite anodes, the next most commonly used ICCP anode material for buried soil applications.

**TABLE 6.20 Properties of High-Silicon Cast Iron and Graphite Anodes**

	Graphite	High-Silicon Cast Iron
Nominal Current Density		
Soil/freshwater, A/m <sup>2</sup> (A/ft <sup>2</sup> )	2–10 (0.2–1)	2–5 (0.2–0.5)
Soil/freshwater, A/m <sup>2</sup> (A/ft <sup>2</sup> )	5–10 (0.5–1)	5–10 (0.5–1)
Soil/freshwater, A/m <sup>2</sup> (A/ft <sup>2</sup> )	5–10 (0.5–1)	10–50 (1–5)
Consumption Rate		
Soil/freshwater, kg/A-yr (lb/A-yr)	0.5–0.9 (1–2)	0.1–0.5 (0.2–1.2)
Soil/freshwater, kg/A-yr (lb/A-yr)	0.1–0.2 (0.2–0.5)	0.05–0.3 (0.1–0.7)
Soil/freshwater, kg/A-yr (lb/A-yr)	0.1–0.3 (0.2–0.7)	0.3–0.5 (0.7–1)
Comments/Limitations	Avoid: Low pH High Sulfate T > 50°C	Avoid: Dry Soils High pH High Sulfate



Graphite anodes contain particulate graphite held together with a light oil impregnation. They were developed in the 1940s and were the most popular ICCP anodes until the development of high-silicon cast iron. Graphite anodes are very fragile, and some users report up to 50% breakage between shipping and construction damage. They are, nonetheless, the preferred anode material for many buried soil applications and, in some parts of the world, their use is greater than any other ICCP anode material. The most common size for these anodes is rods 7.6cm diameter by 150cm long (3in. diameter by 60in. long).

Graphite anodes are almost always used with a carbonaceous backfill which prolongs anode life. The backfill moves the oxidation reaction to the backfill and both prolongs anode life and increases the relative contact area of the anode with the soil environment. Carbonaceous backfill is often supplied with embedded anodes in prepacked perforated steel cylinders that greatly reduce breakage during shipping and construction. The perforations allow the release of gaseous oxidation products, and eventual corrosion of the steel cylinders is acceptable, because they have served their purpose once the anodes are in place in the ground bed.

Table 6.20 compared the properties of graphite anodes with high-silicon cast iron, their primary competitor in most buried in soil applications. One limitation on graphite anodes is that they will disintegrate if the current density is too high. This is caused by a loss of the binder material due to gas evolution within the anode.<sup>96</sup>

MMO anodes were originally developed and marketed in the 1960s for the chemical process industry.<sup>96</sup> They were quickly adapted to cathodic protection. They are the third-most commonly used ICCP anode material for buried soil applications and, in some markets, are the leading ICCP anode for marine applications, although high-silicon cast iron remains competitive.

Their primary advantage in marine applications is their relatively light weight in comparison to high-silicon cast iron. The anodes consist of commercially pure niobium or titanium substrates with proprietary oxide mixtures on the surface. They are available as discs, tubes, and wire. For onshore applications, they are often supplied as tubes with a prepackaged backfill, although they can also be used, for example, in deep well applications (described later in this chapter) with loose carbonaceous backfills. They are available as wire, tubing, rod, strip, and mesh shapes. Life is limited by the oxidation of the substrate metal, and they are usually limited to temperatures less than 40°C (140°F).

MMO anodes have been used for buried applications, but with limited success. The titanium substrates do not work in dry soils, and niobium is not much better.<sup>97</sup> Niobium-substrate MMO anodes do find use for tank bottom protection, where they are inserted between the tank bottom and a liner in a 0.3m (12in.) gravel/sand environment, but this is a very limited application.<sup>96</sup> While titanium substrates have problems in many high-resistivity environments, they have become the standard for use in offshore applications.<sup>98</sup> The breakdown of MMO substrates seems to be dependent on the applied current density.

Table 6.21 summarizes some of the properties of MMO anodes.

While other precious metals can also work as anode surface materials, virtually all precious metal-clad anodes use platinum as the surface material. Precious metal anodes were developed in the 1960s and were initially used in offshore applications where their weight advantages over high-silicon cast iron made them economically competitive. Platinum has a very high exchange current density, approximately 10,000 times higher than high-silicon cast iron.<sup>99</sup> This results in substantial weight savings for the installation of these anodes. The major problem with platinum and other

**TABLE 6.21 Mixed-Metal Oxide Anode Properties**

	Carbon Backfill		Freshwater	Brackish Water	Seawater	Mud Saline
	High Current	Special				
Current Density, A/m <sup>2</sup> (A/ft <sup>2</sup> )	83–140 (7.7–13)	35–40 (3.3–3.8)	83–170 (7.7–16)	83–260 (7.7–24)	480–610 (45–57)	83–240 (7.7–22)
Life, years	20	20	20	15	15	15
Comments:	Above ratings do not apply to Expanded Mesh Anodes. Current densities must be deaerated at temperatures below 5–10°C. Electrolyte impurities can affect ratings. Mixed-metal oxide surface is susceptible to abrasion damage. Attenuation should be considered in long, thin wires and rods.					

Data from Slide 101 NACE CP Technologist Chapter 2, January 2005.

precious metals, which all have similarly high exchange current densities, is their cost. For this reason, most platinum anodes are made by coating a thin layer of platinum onto either a titanium or niobium substrate.

Platinum anodes have been used in a wide variety of applications. Problems with anode breakdown (buildup of a high-resistance oxide film at the platinum–titanium interface) have diminished the use of titanium-substrate anodes in buried applications, and niobium-substrate anodes have similar, but lesser, problems. Platinum anodes remain the fourth most popular anode material for buried onshore applications and they find other uses in process equipment and marine environments. For buried applications, they are typically used with either prepackaged backfills or inserted vertically into deep wells which are then filled with carbonaceous backfills.<sup>96</sup>

Platinum and other precious metals are very soft, and these anodes should not be used in flowing-water situations where abrasion can remove the very thin and fragile platinum surface layer.

Polymer anodes have a very limited market in oil and gas production operations. They are supplied as flexible wires with graphite embedded into the wire insulation. Their use is primarily as distributed anodes in low-current situations such as the ground side of storage tank bottoms and buried in parallel along relatively short well-coated pipelines, for example, in industrial areas and tank farms where conventional ICCP anodes would require more expensive deep wells to avoid stray current problems. They have been in use since the 1980s, and there are reports of premature anode failure due to changes in the resistivity of their environments.<sup>97</sup> Most buried applications call for the anodes to be buried in carbonaceous backfills.

The first applications of ICCP used scrap steel for anodes. This practice diminished with the development of graphite and high-silicon cast iron anodes in the

1940s and 1950s. Scrap steel is still used on occasion for ICCP anodes. The most common situation would be where an abandoned-in-place structure, usually a pipeline, is used as an anode for ICCP of a replacement or newer pipeline in the same right of way. Scrap steel is inexpensive but, unlike the materials discussed above, it is consumed as an anode and has a limited life. Nonetheless, this approach is still used, especially as the original uncoated pipelines constructed in the 1930s through the 1950s are replaced with new parallel pipelines having modern coatings. The small exposed surface area of the new pipelines means that the average applied current density on the abandoned pipelines or gathering lines is very small and the scrap steel anodes should last for many years.<sup>96</sup>

At one time, lead anodes with silver or other precious metal additions were used as very heavy precious metal anodes. These anodes were used before precious-metal cladding techniques were developed. The lead would corrode, leaving an enriched silver or other precious metal surface. These enriched surfaces had high exchange current densities. The heavy weight was useful in locations such as Cook Inlet in Alaska where high tidal currents would damage less robust anodes. The anodes were mounted on sleds that sat on the sea bottom at remote anode bed locations. Like most anode sled arrangements, mechanical damage to the lead wires was a concern. While several NACE and other standards still list these materials,<sup>100</sup> they have not been specified in North America for many years and are not listed by most cathodic protection anode suppliers.

Tables 6.22 and 6.23 summarize information on the use of ICCP anodes in seawater and underground service—the two most common ICCP environments. The advantages of MMO and platinized-titanium anodes for seawater service are apparent. For onshore applications, the weight savings realized by the use of these lighter anodes is much less important, but the

**TABLE 6.22 Impressed Current Anode Material Consumption Rates**

Impressed Current Anode Material	Typical Anode Current Density in Saltwater Service A/m <sup>2</sup> (A/ft <sup>2</sup> )	Nominal Consumption Rate/g/A-y (lb/A-y)
Platinum (on titanium, niobium or tantalum substrate) or titanium mixed-metal oxide	540 to 3320 (50 to 300)	3.6 to 7.3 (0.008 to 0.016) <sup>a</sup>
Graphite	11 to 43 (1 to 4)	230 to 450 (0.5 to 1.0)
Fe-14.5%Si-4.5%Cr	11 to 43 (1 to 4)	230 to 450 (0.5 to 1.0)

Extracted from table C1, NACE SP0176-2007.

<sup>a</sup> This figure can increase when current density is extremely high and in low-resistivity waters.

**TABLE 6.23 Summary of ICCP Anode Properties for Underground Cathodic Protection Systems<sup>95</sup>**

	Graphite	Si-Cr Cast Iron	Mixed-Metal Oxide	Platinum-Coated	Polymeric	Scrap Steel
Consumption rate	0.1 to 1 kg/A-y (0.2 to 2 lb/A-y)	0.1 to 0.5 kg/A-y (0.2 to 1 lb/A-y)	Coating/titanium bond determines anode life	8 to 16 mg/A-y	Projected 20-year life requires installation in carbonaceous backfill	9 kg/A-y (20 lb/A-y)
Current density, maximum	5 A/m <sup>2</sup> (0.5 A/ft <sup>2</sup> )	10 A/m <sup>2</sup> (1.0 A/ft <sup>2</sup> )	100 A/m <sup>2</sup> (9.3 A/ft <sup>2</sup> )	110 A/m <sup>2</sup> (10 A/ft <sup>2</sup> )	52 mA/m (16 mA/ft) (1.3 A/m <sup>2</sup> [0.12 A/ft <sup>2</sup> ])	Unknown
Common shapes	Cylindrical	Tubular and solid cylindrical	Tubular and wire	Wire	Wire	Pipe, rail, and casing
Handling precautions	Material is brittle	Material is brittle	Oxide can be damaged by abrasion	Platinum can be damaged by abrasion	Can be damaged by abrasion	None: anodes are heavy
Connections	Mechanical connections at center or near end of anode	Mechanical connections at center or near end of anode	Mechanical connections at center or end of anode	Brazed or mechanical connections at end of anode	Brazed or mechanical connections	Multiple connections, brazed or bolted
Packaging	Sold bare or in canisters	Sold bare or in canisters	Sold bare, with foam protectors, or in canisters	Sold bare or in canisters	Sold bare or packaged	No packaging
Environmental hazards	None known	None known	None known	None known	None known	None known
Date of first use	1940s	1950s	early 1980s	1960s	early 1980s	1930s
Other notes	Typically fully impregnated with oil, wax, or resin	None	Connection seals for tubular anodes tested by the manufacturer	None	Typically installed in shallow, horizontal beds	Multiple sealed connections allow full use of anode

Table A-1, NACE Publication 10A196 Impressed Current Anodes for Underground Cathodic Protection Systems, NACE 1996.

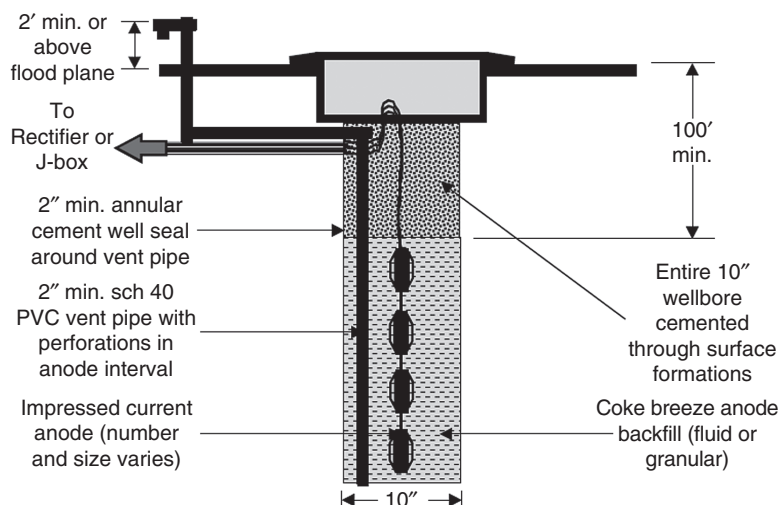
reduced cost of handling and transport of these much lighter anodes remains one of the reasons for their continued and increasing popularity, especially in remote areas where transportation to construction sites is restricted. The relative market share of the top three anode materials for onshore and natural water service is summarized in Table 6.24.

Most ICCP anode materials used in soil applications require, or at least benefit, from the use of backfill materials which surround the anode and provide a more electrically conductive environment. These backfills make the anode environment more electrically conductive, which lowers electric power requirements. They

**TABLE 6.24 Relative Market Share of ICCP Anodes**

Environment		
Soil	Freshwater	Seawater
High-silicon cast iron	Mixed-metal oxides	Mixed-metal oxide
Graphite	Pt/Nb or Pt/Ti	Pt/Nb or Pt/Ti
Mixed-metal oxides to a limited extent, but not in dry soil	High silicon cast iron use is declining	High-silicon cast iron

Data supplied in 2008 by Farwest Corrosion Control for California including offshore and by Deepwater Corrosion Services (Gulf of Mexico and worldwide offshore) in 2008.



**Figure 6.71** Typical deep anode bed in normal soil strata.<sup>102</sup>

also prolong the life of the anode. Carbonaceous materials are almost universally used for this purpose. These materials, either metallurgical coke (manufactured from coal) or similar high-carbon particulate materials with hydrocarbon precursors, extend the life of the anodes and move most of the oxidation reaction, which will eventually degrade the anode, to the backfill particle surfaces. Backfill materials are provided in prepackaged format for some anodes or in bags similar to those provided for galvanic anodes.<sup>96</sup> The relatively low-conductivity soil backfills used for galvanic anodes should not be used for ICCP anodes.

There have been fewer quality control problems with ICCP anode suppliers than with galvanic anodes. Most users rely on preapproved qualified vendors to insure the quality of ICCP anodes.

Deep anode beds are sometimes used for galvanic anodes in locations where right of way restrictions or the lack of shallow groundwater dictate their use. They are much more common in ICCP systems where the stray current problems are more severe because of the relatively large currents normally associated with ICCP rectifiers and multiple-anode ground beds. Figure 6.71 shows a typical deep anode ground bed.

Deep wells require casings—liners for the hole that prevent contamination of groundwater and provide a means for venting the oxidation product gases. If the anodes are located in salty water, the chlorine gases that are liberated will be poisonous, but oxygen is the most common gas generated by most deep wells. Casings for deep wells are often made from PVC—a polymer that is resistant to oxidizing gases. Most cathodic protection deep wells are drilled using similar equipment to that which is used for drilling water wells. The drilling uses



**Figure 6.72** Dielectric shield flush mounted on a hull.<sup>102</sup>

water-based drilling muds that must be thinned before installing the anodes and backfills, which are usually coke breeze or other carbonaceous materials.<sup>102</sup>

The most efficient current distribution is achieved when anodes are located at electrically remote locations. If this is impractical, for example, on floating hulls, then the use of flush-mounted anodes with dielectric shields—insulators placed between the anode and the structure to be protected—becomes necessary. Figure 6.72 shows a dielectric shield flush-mounted on a hull.<sup>101</sup>

Flush-mounted anodes with dielectric shields are relatively inefficient. They distribute more current than necessary near the dielectric shield–structure interface in order to provide adequate current farther away—usually at the midpoints between two anodes. It is important to inspect and regulate the current to flush-mounted anodes in order to prevent coating debonding



caused by excessive cathodic current near the anodes. Figure 6.73 shows coating debonding caused by excessive cathodic current on a flush-mounted anode.<sup>82</sup> These shields are made from a variety of polymeric materials.

The advantages of ICCP cathodic protection include the large electrical current available from one rectifier/anode bed installation, the low installation cost compared to galvanic systems requiring many anodes, and the long life of ICCP anodes if correctly installed and operated in the correct current density ranges. It is not unusual to have rectifiers and associated equipment in continuous operation for several decades with only routine maintenance and occasional anode replacement.

Limitations of ICCP systems include the increased possibility of hydrogen embrittlement of any high-strength (high hardness) steel, for example, at improperly welded joints, and the increased likelihood of causing coating debonding or stray current corrosion on nearby structures. Highly trained maintenance and inspection personnel (usually the same people) are also required because of dangers associated with maintenance on rectifiers and to prevent reversed polarity connections at rectifiers. The relatively high maintenance and trained personnel requirements of ICCP systems are why most offshore cathodic protection systems use galvanic anodes.

**Comparison of Galvanic Anodes and ICCP** Table 6.25 compares galvanic anode and ICCP systems.

The installation of a galvanic anode is fairly inexpensive, and it is possible to install anodes for under \$100 per anode if the structure is already exposed. This low

initial cost plus the low maintenance/inspection costs make galvanic anode cathodic protection the option of choice for many oilfield applications.

### Cathodic Protection Criteria

Operators of cathodic protection systems need to be able to determine if the structures are being adequately protected. Figures 6.63 and 6.64 showed that the corrosion rate is substantially reduced whenever the structure potential is shifted in a cathodic direction. The question then becomes how much cathodic protection is desired or necessary.

Early proponents of cathodic protection discussed criteria for cathodic protection. Some advocates suggested that cathodic protection needed to approach the equilibrium potential. Others suggested that a potential shift of any amount would yield prolonged life and over-protection was costly.

The first international standard on cathodic protection, NACE RP 0169 (now termed SP0169), listed the following means of determining if cathodic protection had been achieved:<sup>102</sup>

- $-850\text{ mV}$  polarized potential
- $100\text{ mV}$  polarization
- $300\text{ mV}$  shift
- $E \log i$
- Net protective current

Recent revisions have eliminated some of these criteria, and the validity of the remaining criteria remains controversial.



**Figure 6.73** Coating debonding caused by excessive current from a flush-mounted anode.<sup>83</sup>

**TABLE 6.25** Comparisons between Galvanic Anode and Impressed Current Cathodic Protection Systems

System	
Galvanic Anode	Impressed Current
Low initial investment for small systems	Cheaper for large systems
Fixed voltage	Adjustable voltage
Small voltage	Small to large voltages
Fixed current	Adjustable current
Small current	Small to very large currents
Low maintenance	Higher maintenance
Stray currents unlikely	Stray currents possible
Reversed potentials impossible	Reversed polarity possible
No power source necessary	Requires external power
Excess current unlikely	Excess current can cause coating debonding

**–850 mV CSE Criterion** Over the years, many authorities came to the conclusion that the –850 mV CSE potential advocated by R. Kuhn and his colleagues in Louisiana was the easiest and most reliable way to determine if cathodic protection had been achieved. This idea was incorporated into the first international standard on cathodic protection, NACE RP0169 (since changed to SP0169).<sup>102</sup> Mr. Kuhn's arguments were based on leak records that showed that if cathodically protected structures were kept at –850 mV or more compared to CSE, then leaks due to corrosion were substantially eliminated.<sup>76–79,103,104</sup>

This approach was reinforced by Peabody, who published a practical galvanic series of metals in soil in 1967 (Table 6.26).<sup>103</sup> This showed that carbon steel (“mild steel” in Peabody's terminology) would have a native, or unprotected, potential of somewhere between –0.2 and –0.8 V CSE. Thus, Kuhn's recommended potential of –0.85 V (–850 mV) is at least a 50 mV shift in the cathodic direction, and usually much more. Peabody and Parker were the two standard references on cathodic protection of pipelines in 1969 when NACE RP169 was first published, and both books advocated the –850 mV criterion, although they do discuss other criteria for determining if cathodic protection has been achieved.<sup>103,104</sup>

Many authorities pointed out, and still do, that it is unnecessary to have steel at –850 mV CSE in order to achieve cathodic protection.<sup>105</sup> While this has always been the case, most owner operators choose to use the –850 mV criterion in NACE SP0169 and similar standards, because it is easy to measure and to train inspectors on how to perform the necessary measurements. Electricity is generally cheaper than trained labor, which is necessary to inspect according to the other, more complicated, criteria.

In cases where microbially influenced corrosion (MIC) is suspected or at elevated temperatures, the protection potential is considered to be –950 mV CSE.<sup>79,85,102</sup>

**TABLE 6.26 Practical Galvanic Series**

		Volts
Metal		(CSE)
Noble or cathodic	Copper, brass, bronze	–0.2
	Mill scale on steel	–0.2
	Mild steel (rusted)	–0.2 to –0.5
	Mild steel (clean and shiny)	–0.2 to –0.8
Active or Anodic	Zinc	–1.1
	Magnesium	–1.75

Note: Condensed from Table 2.2 in Peabody, *Control of Pipeline Corrosion*.<sup>103</sup>

Little controversy has appeared over the idea of a similar criterion for locations where MIC is suspected. The change of potential to –950 mV due to temperature is not controversial and can be understood by anyone who considers the Nernst equation, developed long before cathodic protection was common, that clearly explains why electrode potentials for any reaction will be affected by temperature. This is in contrast to the continuing controversy over the necessity to use an “instant off” or similar IR-compensation technique to identify the “true” potential of a structure.

All of the above discussion has related to buried structures, primarily pipelines. Other reference electrodes are used in different applications. The corresponding voltage for silver-silver chloride electrodes, which are used in seawater, is –805 mV, although this is usually rounded to –800 mV.<sup>100</sup>

**–100 mV Shift Criterion** Advocates of the –100 mV shift criterion point out that –850 mV CSE is not necessary to achieve cathodic protection (an acceptable reduction in corrosion activity) in many, perhaps most, cases.<sup>105,106</sup>

They also claim that in some circumstances –850 mV CSE, however determined, may not produce protection. This latter claim is very controversial and, except in the cases of elevated temperature, parallel zinc anodes, or microbial activity, it has not been unequivocally documented.

The –100 mV shift criterion assumes that unshifted potentials can be determined. This is impractical for galvanic anode systems. It also assumes that the unshifted (or native) potential of the structure does not change with time. Areas with changing groundwater levels due to seasonal wet and dry seasons are one example of where native (unprotected) potentials are likely to change.

Turning off ICCP systems to determine the native potential requires up to 48 h for the potential to decay to the unshifted potential.

The difficulties and limitations discussed above have led most operators to prefer to use the –850 criteria for determining cathodic protection.

**E Log i Criterion** There are structures where it is inconvenient or impossible to place reference electrodes along the structure being protected. Well casings are an excellent example of this situation. While the top of the well casing is available for electrical connections, the bottom of the casing is inaccessible. The E log i criterion (Tafel curve method) is used in these situations to measure the current necessary to provide cathodic protection.

Figures 6.74 and 6.75 show how this is done. A cathodic current source is connected to the casing and current is applied. The potential at the casing head is measured before the current is applied and the change in potential is monitored as additional cathodic current is applied to the casing.

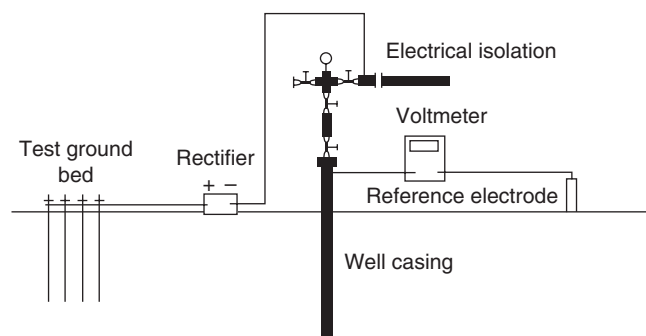
At the corrosion potential no current is being supplied from the external power supply, and the corrosion potential,  $E_{\text{corr}}$ , is due to the natural oxidation and reduction reactions on the structure. The total oxidation and reduction currents are unknown. As current is supplied from an external power source, the potential versus log of applied current plot begins to curve downward when the applied current is similar in magnitude to the natural current. Increased applied current leads to a situation where virtually all of the cathodic current is coming from the power supply. The plot then becomes linear or straight. The applied current where the potential-log current plot becomes “straight” or linear is assumed to be the current necessary to provide adequate cathodic protection. At one time, it was suggested that the “linear” portion of the  $E \log i$  plot should extend over one decade (or order of magnitude) of current. In recent years, a two-decade (100-fold change in current) linear region has been recommended.<sup>107–109</sup>

The current requirement from the  $E \log i$  method is considered conservative, and leak records seem to confirm that idea.<sup>110–112</sup>

The  $E \log i$  or Tafel extrapolation method can also be used to determine the corrosion current. This is discussed in Chapter 7, Inspection, Monitoring, and Testing.

### Inspection and Monitoring

The continued operation of cathodic protection systems requires monitoring to insure that the system is working adequately. Third-party damage, coating degradation leading to increased current demands, changes in environment, and ageing of cathodic protection components

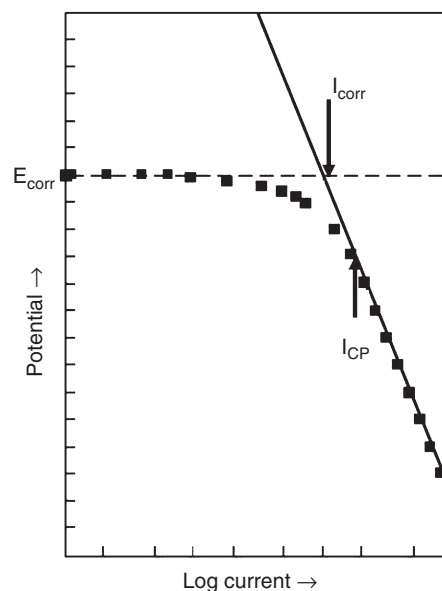


**Figure 6.74** Test setup for  $E \log i$  testing to determine the necessary cathodic protection current for a well casing.<sup>112</sup>

can all cause systems to degrade. There are many inspection and monitoring methods used in conjunction with cathodic protection. This section only discusses some of the more important methods. More complete discussions are available.<sup>78,106–118</sup> Inspection and monitoring is required on at least an annual basis for most pipeline systems in the United States, and more frequent intervals are sometimes necessary. Rectifier operations must be monitored every 2.5 months in the United States.

**Potential Surveys** The most common means of inspecting a cathodically protected structure is by means of a potential survey. In any potential survey, it is necessary to measure the potential of the structure in question relative to a standard potential. The most commonly used reference electrode is the saturated copper-copper sulfate electrode (CSE), which is used onshore and in freshwater applications. This is shown in Figure 6.76. Silver-silver chloride electrodes are used in marine applications, and the conversion from one standard to the other is fairly simple. The  $-850 \text{ mV}$  CSE standard theoretically becomes  $-805 \text{ mV}$  with the silver-silver chloride electrode, but it is usually rounded to  $-800 \text{ mV}$ . Zinc is sometimes used as a robust reference anode for permanently mounted test stations on offshore structures.

Reference electrodes can degrade and must be maintained.<sup>119</sup> It is common for inspectors to carry three electrodes with them. Two are used and checked against each other. If they do not produce the same result, they are then checked against a “less weathered” electrode



**Figure 6.75** Plot of  $E \log i$  data for a well casing.

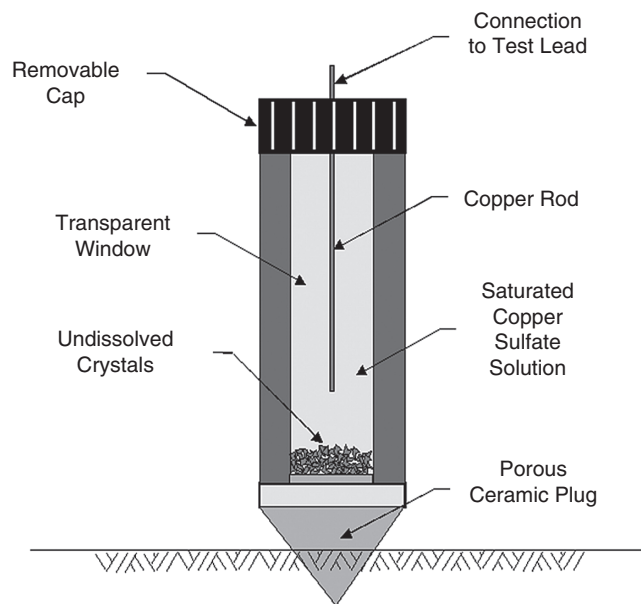
in the hopes that one or the other electrode will still be in calibration.

In order to measure the potential of a structure, it must be connected through a high-impedance voltmeter to a reference cell in direct electrical contact with the same electrolyte. This is shown in Figure 6.77.

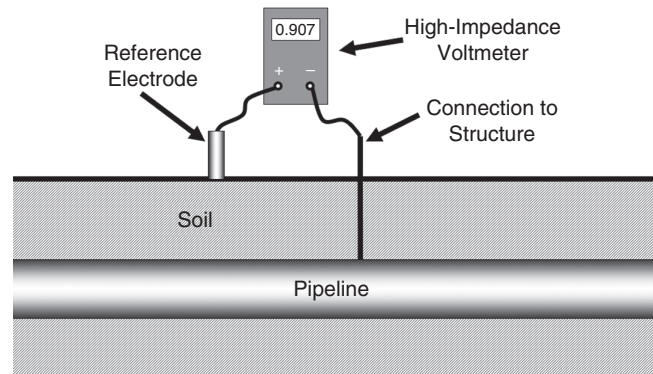
At one time, it was common for pipeline surveyors to make electrical connections with the buried pipeline by driving a pointed rod into the soil over the pipeline. This caused unnecessary coating damage. It is now more

common to locate test points along the right of way. These test points are electrical connections to the pipeline and allow the surveyor to make electrical connections to the pipeline without damaging the coating. A secondary advantage of using test points is that they are permanent locations and insure that connections on subsequent surveys will be made at the same location. A typical flush-mounted test point is shown in Figure 6.78.

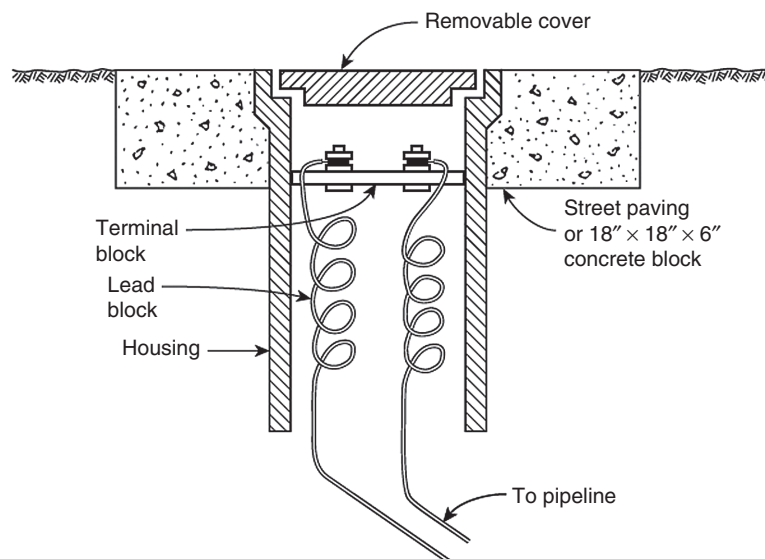
Test stations of this type are available from most cathodic protection equipment suppliers. The at-grade design has the advantage of being less likely to suffer vandalism or other third-party damage. It is, however, hard to find and is subject to being covered over by soil erosion. Above-ground designs are also available. The minimum spacing for test stations is at the midpoint between anode locations, the most likely location for



**Figure 6.76** Saturated copper-copper sulfate electrode.



**Figure 6.77** Measurement of pipe-to-soil potential.



**Figure 6.78** Typical at-grade test station.<sup>114</sup>



the pipeline potential to be unprotected. These test stations are often required by regulatory agencies, and their locations are recorded on maps of the cathodic protection system. It is possible to instrument these test points and relay the readings to remote locations.

Test points on cross-country transmission pipeline are typically located at intervals up to several kilometers (miles) and at cased road crossings, wherever they cross another utility, and at buried insulated joints.

Pipelines run for long distances, and the most common surveys are over-the-line close-interval potential surveys (CIPS) where the surveyors follow the right of way and make measurements at predetermined intervals. This is shown in Figure 6.79. The intervals between readings can vary but are typically in the hundreds of meters (yards) for many cross-country pipelines. These surveys supplement the information obtained from readings at the test points, which usually are spaced much farther apart.

A typical pipe-to-soil potential profile is shown in Figure 6.80. Virtually all cathodic potentials are negative, and it is common to plot the larger negative voltages higher on the vertical axis. As long as the potential is more negative than  $-850\text{ mV CSE}$ , most authorities will consider the pipeline to be protected. The problem areas identified by this survey are shown near the center of Figure 6.79 where the negative voltages are less than  $-850\text{ mV}$ . The problem could be caused by a disconnected magnesium anode or by other factors. Once the

unsatisfactory potential survey results are available, it is usually necessary to inspect the pipeline in these locations in greater detail to determine the source of the problem.

**Resistivity Surveys** Soil resistivity is commonly measured when planning ICCP ground-bed locations or when determining the corrosivity of pipeline rights of way. The most accurate method is the *in situ* Wenner four-pin method, which has been the industry standard for over 50 years. The Wenner method has the advantage of measuring the average soil resistivity at a depth determined by the pin spacings. Thus, it can measure, without disturbing the soil, the resistivity near the surface, frequently high due to drying between rainfalls, and at the depth of the proposed structure.

The setup for this measurement is shown in Figure 6.81. Four electrical contact pins are placed in the soil surface. An AC electrical current is applied between the outer pins to produce current flow through the soil. The voltage measured between the inner pins is used to calculate resistivity. The four pins are arranged in a straight line, and the distance between pins is adjusted to reflect the depth of the soil of interest. Once the measurements have been made, it is easy to calculate the average resistivity of the soil at the depth equal to the pin spacing. Adjusting the pin spacing allows determination of changes in resistivity with depth.<sup>113,115,116</sup>

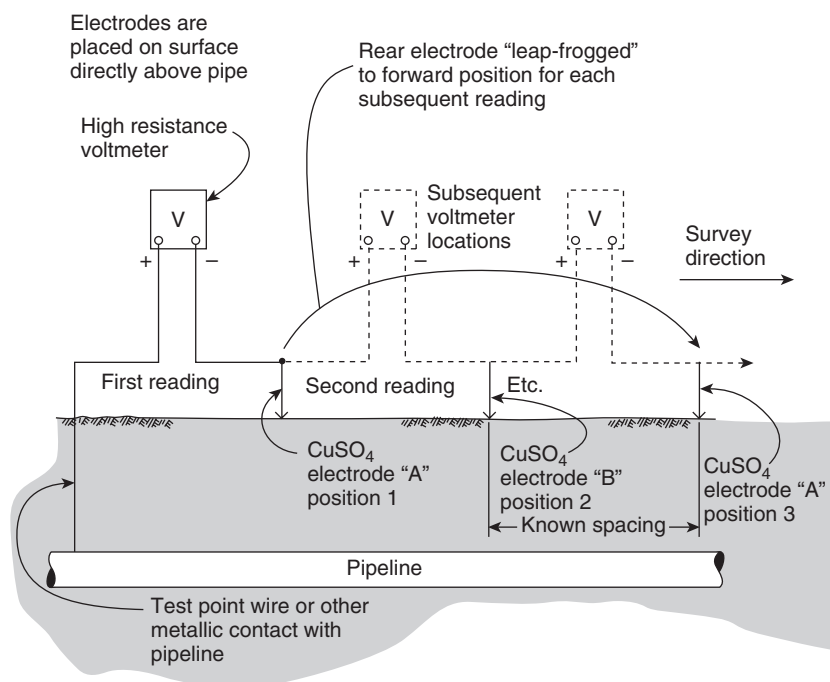
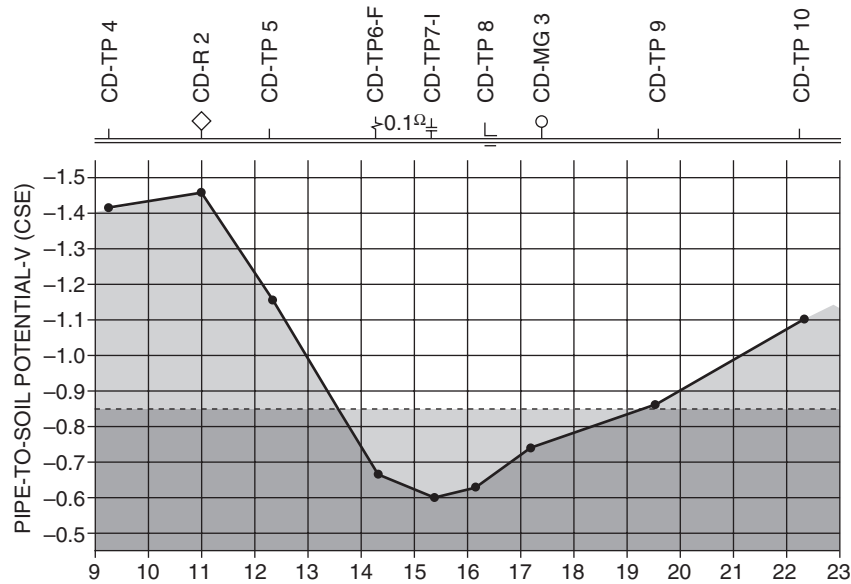
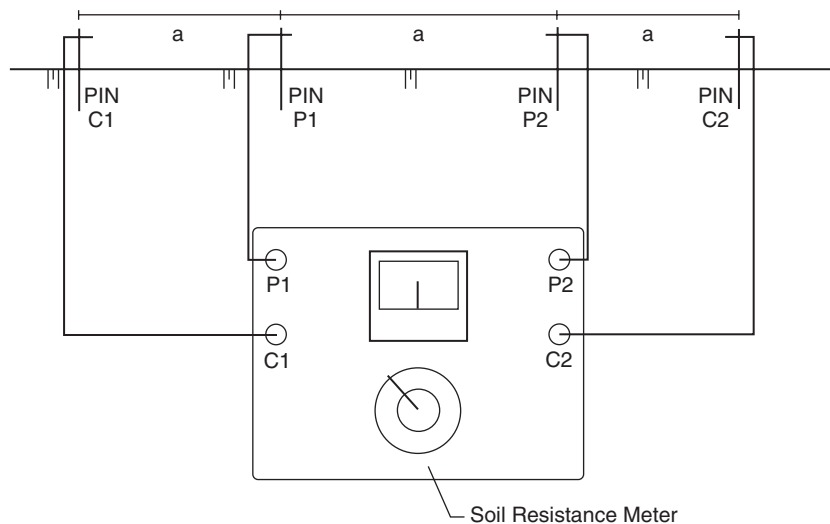


Figure 6.79 Over-the-line potential survey setup.<sup>118</sup>



**Figure 6.80** Protective potential profile indicating a lack of protection near the center of the plot.<sup>116</sup>



**Figure 6.81** Wenner four-pin soil resistivity measurement.<sup>113</sup>

The soil resistivity is calculated from the following formula:<sup>118,122</sup>

$$\rho = 2\pi AR \quad (\text{Eq. 6.9})$$

where:

$\rho$  = soil resistivity (ohm-centimeters)

$A$  = distance between pins

$R$  = resistance measured with the ohmmeter

Most commercial instruments for measuring resistivity automatically calculate the resistivity based on pin spacing and measured resistance.

Changes in resistivity are often indications of changes in moisture levels. Low-lying riparian areas, often with more vegetation, are typical examples of where the resistivity would be lower and expected corrosion rates would increase. Some locations have widely varying soil resistivities depending on the time of the year.

It is sometimes desirable to measure the maximum conductivity (reciprocal of resistivity) by placing the soil from the appropriate depth into a soil box with four-pin connections. The four-pin method is then used to determine the conductivity of the wetted soil. This method cannot determine the effects of soil compaction on conductivity and is not as reliable as the *in situ* four-pin measurements described above.

Single-probe conductivity measurement is also possible. This is less work but is less accurate; only the conductivity at the depth of the local probe is determined at the precise location where the probe is placed.

### Cathodic Protection Design Procedures

Most of the following discussion will emphasize design of cathodic protection systems for pipelines. The *Handbook of Cathodic Protection* contains complete chapters on cathodic protection of ships (applicable to designs for spar platforms and floating production, storage, and offloading [FPSO] structures or vessels), marine structures, well casings, water tanks and boilers, and process equipment.<sup>117</sup>

The first step in any cathodic protection design is to determine the total electrical current demand. For existing structures, this can be done by measuring the current necessary to produce the desired potential shift. This is done by connecting the structure to a temporary DC power source and varying the current until the necessary polarization, determined by either the E log i method or by simple measurement of the potential at remote locations from the temporary anodes. The choice of method depends on whether or not the remote location is accessible for potential measurement. In either case, it is necessary to wait until changes in the applied current have produced steady-state potentials before increasing the current to the next level. This can take minutes to hours depending on the size of the structure involved.

New pipeline cathodic protection design is often based on the current expected to be necessary after 20 years of service. The coating degradation is not expected to worsen after that period of time. Designs provide more current than is necessary during the early life of the system and are intended to last indefinitely. For this reason, it is common to overdesign the system, because it is easier, and is supposedly less expensive, to install a somewhat larger than necessary system at the beginning than it is to retrofit at some later date. Most authorities recommend current densities based on expected bare metal exposed area. Sometimes the assumption is that 1% of the possible surface area will be exposed, but this is seen as very conservative for some of the newer pipeline coating systems. Tables 6.27 and 6.28 show guidelines from several different oil companies' published recommendations for the minimum current densities necessary for buried pipeline cathodic protection.<sup>117</sup> The effectiveness of high-quality coatings is obvious from the reduced current demands shown for FBE and polyethylene.

Once the current requirements have been identified, the design procedure then must consider a number of

**TABLE 6.27 Recommended Minimum Cathodic Protection Design Current Densities for Different Soils<sup>117</sup>**

Soil resistivity ohm.m	Design Current Density mA/m <sup>2</sup> (bare steel)
<10	20
10–100	10
100–1000	5
>1000	1

Note: A 2.5% increase for each degree C rise above 30°C.

**TABLE 6.28 Recommended Minimum Cathodic Protection Design Current Densities for Different Soils<sup>117</sup>**

Coating	Design Current Density mA/m <sup>2</sup>
None	20
Tape wrap	1.25
Coal tar epoxy	0.75
FBE	0.1
Polyethylene	0.1

alternatives based on the choice of anode type. Figure 6.82 is one of a number of recommended design procedures that are available.

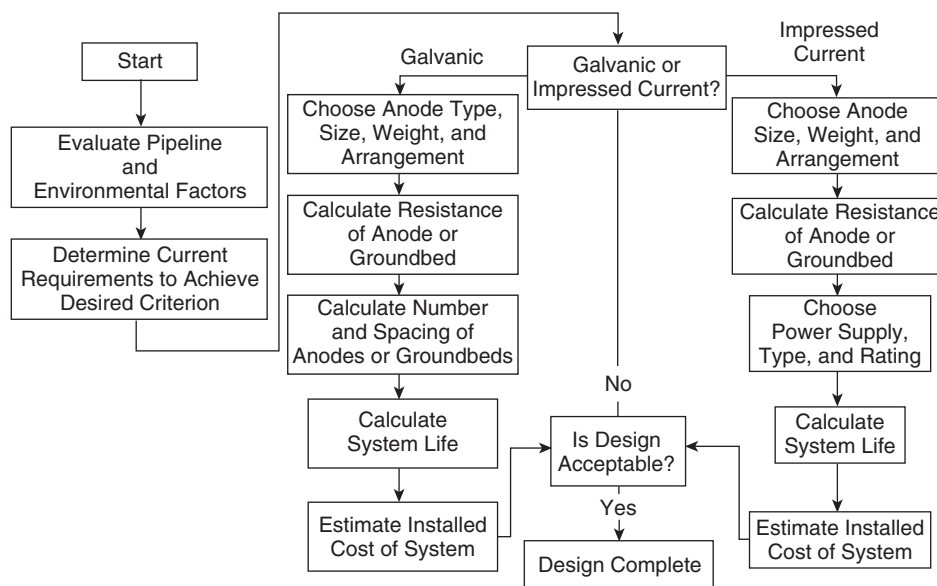
The procedures for calculating all of the above design steps have been standardized for many years. Many of the necessary formulas, for example, for calculating ground-bed resistance, are based on work done in the 1930s. While the calculations can be done by hand (as they were originally), it is more common to do them using computer software. Most of this software is based on spreadsheets, and many cathodic protection contractors have developed their own in-house software for this purpose. In recent years, several websites have become available that do these calculations. Figures 6.83 and 6.84 are examples of what is available. As the use of computers increases, this kind of user-friendly software will become more common.

For many years, the 1960s' book, *Control of Pipeline Corrosion* by A. W. Peabody, was considered to be one of the premier reference materials on cathodic protection.<sup>103</sup> The book was updated in 2001, and the compact disc that accompanies the updated book has spreadsheet-based software included. Figure 6.85 is one example of the screens used by the compact disc that accompanies this widely used handbook.

The compact disc also contains sample problems showing the following calculations:

- Determining protective current requirements
- Anode resistance to earth
- Conventional ground-bed design

### Sample Cathodic Protection Design Procedure



**Figure 6.82** Cathodic Protection Design Procedure. Adapted from NACE International CP Technology Course Slide5/140.

### Cathodic Protection Design for Underground Pipes Using Magnesium Anodes

formulas
 example

**Distributed Anode Design**

Pipe Length = 6500 ft.

Pipe Diameter = 8 in.

Coating Quality = 95%

Current Density = 1 mA/sq.ft.

Soil Resistivity = 2500 ohm-cm.

**Multiple Anode Groundbed Design**

Anode Type = High Potential Magnesium

Anode Size = 17D3 17 lbs.

Design Life = 20 yrs.

#### Calculated Quantities

Surface Area = 14670 sq. ft.	Anode Quantity = 15
Anode Spacing = 434 ft.	Expected Life = 16.01 yrs.
Current Requirement = 0.734 amps	Expected Polarized Potential = 0.901 volts
Output Current = 0.773 amps	

**Recommendations**

The above 15-anode system design uses the minimum number of anodes to produce enough current to satisfy the current requirement. Expected life of the system is 16.01 years which is less than the design life. In an attempt to satisfy both current requirement and design life an additional design is presented below.

Surface Area = 14670 sq. ft.	Anode Quantity = 18
Anode Spacing = 362 ft.	Expected Life = 20.01 yrs.
Current Requirement = 0.734 amps	Expected Polarized Potential = 1.192 volts
Output Current = 0.742 amps	

**Recommendations**

**Figure 6.83** Online screen for calculating galvanic anode life. Image courtesy of Mesa Products, Inc., <http://www.mesaproducts.com> and [http://www.cpdesigncenter.com/public/cp\\_calculators/currentrequirement.htm](http://www.cpdesigncenter.com/public/cp_calculators/currentrequirement.htm), May 2, 2010.



Current Requirement					
<input type="radio"/> Pipe		<input checked="" type="radio"/> AST		<input type="radio"/> UST	
Diameter =	100 ft.	Length =	30	ft.	
Coating Quality =	90%	Current Density =	1 mA/sq.ft.		
UST Head Geometry					
Head 1:	<input checked="" type="radio"/> none	<input type="radio"/> flat	<input type="radio"/> hemisphere		
Head 2:	<input checked="" type="radio"/> none	<input type="radio"/> flat	<input type="radio"/> hemisphere		
Calculate			Reset		
Surface Area =	7853.98	sq.ft.			
Current Requirement =	0.7853982	Amps.			

\* Appropriate unit conversions are performed by the program.

\*\* Coating quality is the percentage of the structure protected by coating.

Formula Used:

$$R = \frac{Sd(1 - q)}{1000}$$

Where

R = current requirement in amps

S = surface area in sq.ft.

d = current density in mA/sq.ft.

q = coating quality as a decimal

**Figure 6.84** Online screen for calculating total current requirement for cathodic protection of pipelines or storage tanks. Image courtesy of Mesa Products, Inc., <http://www.mesaproducts.com> and [http://www.cpdesigncenter.com/public/cp\\_calculators/currentrequirement.htm](http://www.cpdesigncenter.com/public/cp_calculators/currentrequirement.htm), May 2, 2010.

NACE  
Companion to the Peabody Book  
October 26, 2000  
Revision 1.1M

Dwight's Equation for Single Vertical Anode Resistance to Earth - millimeters

$$R_V = \frac{1.59 \rho}{L} \left( \ln \frac{8L}{d} - 1 \right)$$

$\rho$  = Soil resistivity in ohm-cm

$L$  = Rod length in mm

$d$  = Rod diameter in mm

$R_V$  = Resistance of vertical rod in ohms

$\rho$  = 10,000 ohm-cm

$L$  = 2134 mm

$d$  = 203 mm

$R_V$  = 25.6 ohms

Dwight's Equation for Single Vertical Anode Resistance to Earth—meters

$$R_V = \frac{0.00159 \rho}{L} \left( \ln \frac{8L}{d} - 1 \right)$$

$\rho$  = Resistivity of backfill material (or earth) in ohm-cm

$L$  = Length of anode in meters

$d$  = Diameter of anode in meters

$R_V$  = Resistance of one vertical anode to earth in ohms

$\rho$  = 10,000 ohm-cm

$L$  = 2.13 m

$d$  = 0.203 m

$R_V$  = 25.6 ohms

**Figure 6.85** Screen from CD accompanying Peabody's Control of Pipeline Corrosion, 2nd edition.<sup>118</sup>

- Deep anode bed design
- Cathode resistance to earth
- Total DC circuit resistance
- Current attenuation
- System life of galvanic anode systems

They allow the user to input the data in metric or U.S. conventional units.

**Temperature Effects on Cathodic Protection** Chemical reactions associated with corrosion are highly temperature dependent. Many design guidelines contain advice

on increasing current density for above-ambient temperatures. The consumption rate of anodes depends on temperature, and this must be considered in cathodic protection design and replacement scheduling. The increased consumption rates of anodes can be minimized by using remote anode locations in cooler environments, but this leaves some designs more prone to mechanical damage due to soil movement and other causes.

### **Computer-Aided Cathodic Protection Design**

Computer-aided cathodic protection designs for offshore structures have been tried by several organizations in recent years. These computer-aided designs are of two types:<sup>82,119,120</sup>

- Personal computers used to make the types of calculations (such as the wetted surface area calculations discussed above) that have commonly been used for cathodic protection design. The computer is a time-saver in these calculations and allows a greater number of alternatives to be considered, but the actual design methodology is not changed.
- The use of numerical techniques, such as finite element, finite difference, or boundary integral, to model the potential current distribution around a structure. Initial efforts to use these techniques found limited acceptance because of the time delay caused by communications difficulties between the

operator, the cathodic protection designer, and the computer expert.

The increased memory capabilities of personal computers now allow design engineers to make calculations once requiring mainframe computers. Figure 6.86 shows a sample plot of the cathodic protection on an offshore platform node. The various color arrangements or shadings allow quick assessment of areas that might be inadequately protected.<sup>82,119,120</sup> Comparisons of plots for different anode arrangements allow the designer to quickly determine which anode locations are the most effective and where inspection points should be located to determine if adequate cathodic protection is being achieved at high-stressed node welds and other critical locations.

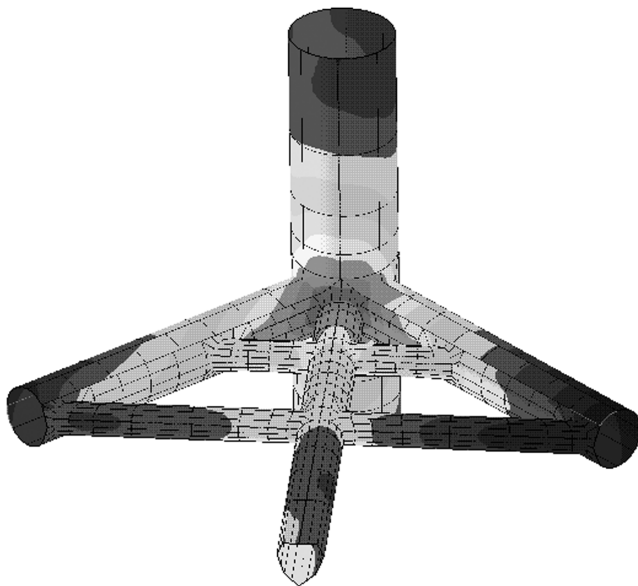
### **Additional Topics Related to Cathodic Protection**

Some of the problems associated with cathodic protection include stray current corrosion, hydrogen embrittlement and stress corrosion cracking of high-strength (or high-hardness) steel, and cathodic disbondment of coatings. In addition to these well-documented problems, many authorities have questioned the standards used over recent decades for determining if a structure is cathodically protected.

**“Instant-Off” Potentials** In recent years, the biggest controversy in cathodic protection has been over the idea of measuring “instant-off” potentials to determine if a structure is protected from corrosion. There are many publications pro and con on this subject, and the ideas behind “instant-off” potentials are the subject of continuing debates.

The first advocates of “instant-off” potentials cited the need for accounting for IR drops between the structure and the electrolyte. This was based on the mistaken assumption that the  $-850\text{ mV}$  CSE potential was the “equilibrium potential” for carbon steel in soil. This is not the case because:

- The  $-850\text{ mV}$  criterion came from leak records and measurements of “current-on potentials” on cathodically protected pipelines, primarily on the Gulf Coast of the United States. R. Kuhn from Louisiana was the most prominent early advocate of this idea, and he based his reasoning on leak records that showed that structures held at potentials at least as negative as  $-850\text{ mV}$  CSE had much lower leak records than unprotected steel. This standard was considered acceptable for most situations, although a  $-950\text{ mV}$  criterion was generally recommended when microbial activity was likely.<sup>76,77,79,85</sup>



**Figure 6.86** Computerized model of the cathodically protected region around a node on an offshore platform.<sup>126,127</sup> Reprinted with permission of ASM International. All rights reserved, <http://www.asminternational.org>.

- The  $-850\text{ mV}$  criterion is at a lower (smaller) negative number than the equilibrium potential. This was shown in Figure 6.64 where the equilibrium potential is shown at  $-950\text{ mV}$  in an acid environment. The equilibrium potential will vary with pH in accordance with the Nernst equation discussed in earlier chapters, but the equilibrium potential will always be at a greater negative potential than the  $-850\text{ CSE}$  protection potential used for cathodic protection. As stated previously, cathodic protection does not eliminate oxidation or corrosion on a protected structure, but it has been shown to significantly reduce corrosion.

In the decades after the NACE RP 0169 standard was adopted, many authors discussed errors in potential measurement, but these errors were considered to be insignificant in most cases.<sup>79</sup>

The IR drops that were originally considered to be insignificant for bitumastically coated pipelines protected with galvanic anodes were questioned for impressed current systems and for measurements directly over galvanic anodes.<sup>108</sup> This led to the development of NACE RP 0169 (92) which mandated that IR drops must be compensated for using an “instant-off” criterion. Difficulties in defining how this “instant off” should be done, and questions on whether or not this “instant-off” potential is necessary, continue as of this writing. Since the requirement to determine an “instant-off” negative potential means that the negative “current-on” potential will be greater than the negative “instant-off” potential, the requirement is conservative. It is, nonetheless, questioned by many and is unpopular with field personnel.

Figure 6.87 illustrates the concept of the “instant-off” method of determining IR errors in cathodic protection. When the cathodic protection current is applied, the structure assumes a potential which is intended to reduce corrosion. In order to measure the potential, a voltmeter is connected to the system and the current-on potential is measured. The measured potential includes the potential of the structure and any current-resistance (IR) drops in the circuit, for example, the reference electrode-electrolyte IR drop and the structure-electrolyte IR drop. By turning off the current, the voltage supposedly “instantaneously” drops to the potential of the structure in the electrolyte. The potential then decays to the unprotected potential, a process that can take anywhere from minutes to days. Proponents of the “instant-off” method suggest that the “instant-off” potential must satisfy whatever criterion, either  $-850\text{ mV CSE}$  or  $-100\text{ mV}$  potential shift, is used for the system. The IR drop can be as large as  $1\text{ V}$  in some instances.

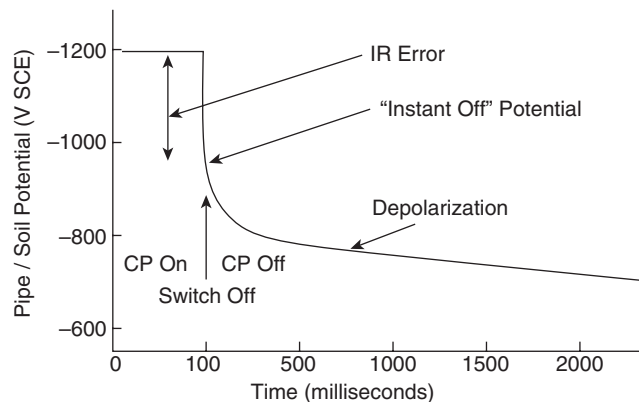


Figure 6.87 Idealized instant-off potential plot.

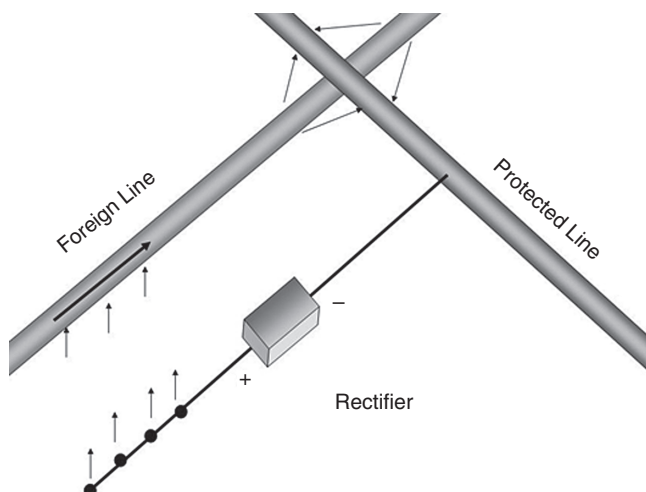
Proponents cite electrochemistry textbooks which identify several IR drops in an electrochemical circuit and the supposed failures of the “current-on” criterion that had been in use for several decades. Opponents of this concept argue that measuring the potential with the current applied has worked for decades. The original “current-on” criterion was developed for onshore pipelines along the Gulf Coast of the United States, a region where soils generally have low resistance. The IR drop of concern is more likely to be of concern with high-resistivity environments. The length of time (from microseconds to several seconds) of the “instant decay” depends, at least in part, on the environment and must be empirically determined.<sup>108,121,122</sup>

**Stray Current Corrosion Caused by Cathodic Protection Systems** The potential field around a cathodically protected structure can cause stray current corrosion on nearby structures. This is a significant problem with ICCP systems that share rights of way with nearby structures/utility systems. Galvanic anodes, with their much lower driving potentials, are unlikely to cause this problem.

Figure 6.88 shows two pipelines crossing each other. The cathodic protection system is causing corrosion where current from the cathodic protection system leaves the unprotected line.

Stray or interference current is detected by turning the cathodic protection system on and off and monitoring the potential of the unprotected line. If the potential of the unprotected line varies with the cycle of turning the cathodic protection system on and off, then stray current corrosion will occur.

Stray current corrosion can usually be handled by bonding a short section of the unprotected line to the protected line and using current from the cathodic protection system to protect both structures. “Hot spot”



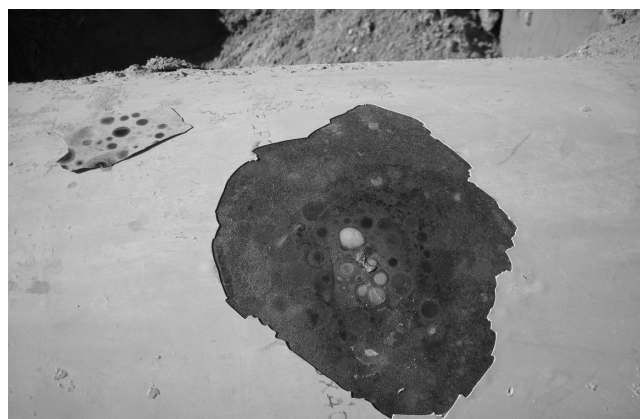
**Figure 6.88** Stray current corrosion on an unprotected line crossing a cathodically protected line. The arrows show current paths from the anode bed through the nearest portion of the foreign line and then leaving the foreign line near the protected line and causing corrosion.

galvanic anodes can also be attached near the location where interference is occurring. These anodes can have the effect of shifting the potential to a protected level. It is also possible to use insulating joints or to adjust the output of the “offending” rectifier to a level where the stray current is reduced. Improvements in the coating on the foreign line are also helpful.<sup>123</sup>

Stray current effects may also be due to natural electromagnetic phenomena. Telluric currents can be identified by recording the pipe-to-soil potential for 24 h. If no recognizable pattern is identifiable, then the currents are probably not man-made and are telluric. These “telluric currents” can have a number of causes, but they normally have minimal effect on corrosion because they usually do not last very long.<sup>123</sup>

**Debanded Coatings** Coating debonding can be caused by excessive cathodic protection or by inadequate coating-to-metal adhesion, which is usually due to poor surface preparation prior to the coating process.

Excessive cathodic protection can cause hydrogen gas evolution at the metal-coating interface. Gas pressure buildup eventually leads to coating debonding. This was shown in Figure 6.72. Some organizations try to avoid hydrogen blistering by limiting the negative potentials allowed for cathodic protection, but the current density at the metal surface is more important. Water is only stable over a 1.23 V range between oxygen evolution at anodes and hydrogen evolution at cathodes. International standards for testing coatings for cathodic debonding resistance use galvanic anodes to



**Figure 6.89** Whitish deposits underneath debonded fusion-bonded epoxy coating. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

test for this phenomenon, and these galvanic anodes can achieve high current densities near coating holidays but very limited potentials. Cathodic protection also shifts the pH at cathodes to more alkaline (higher pH) values, and some coatings are not resistant to debonding in the presence of alkalis.

Coating debonding due to poor surface preparation is shown in Figure 6.89, where an FBE coating has lifted from the surface. The metal underneath the debonded coating is discolored, but no significant corrosion has occurred. The whitish deposits underneath this debonded coating show that cathodic protection has reached the metal surface, increased the pH of the moisture at the metal–environment interface, and caused these mineral deposits, similar to those shown in Figure 6.66.

Debanded coatings lifted away from the metallic substrate can act as dielectric shields preventing cathodic protection currents from reaching the shielded metal surface, and the unprotected metal surface can corrode. FBE coatings have the reputation for not causing this kind of shielding. Other commonly used pipeline coatings do shield the metal surface and allow corrosion to occur as is shown in Figure 6.90. This pipeline, which had substantial areas of debanded coatings, was found to be corroding along much of the pipeline, even though cathodic protection was applied and above-ground pipe-to-soil readings indicated that the structure was cathodically protected.

Dielectric shielding masks the problems of corrosion underneath the coating, and this unprotected area cannot be identified by potential measurements using close interval surveys or other commonly used over-the-ground pipeline inspection techniques. This type of





**Figure 6.90** Pitting due to debonded coating which shielded cathodic protection current. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

coating disbonding can increase cathodic current demand by increasing the total surface area of uncoated metal.<sup>124</sup>

**Misapplication of Galvanic Anodes on Small Underground Storage Tanks** Many owners of underground storage tanks are small operators with no professional corrosion staff or experience. The Steel Tank Institute in the United States developed STI p3 tanks to meet this market (Figure 6.91). They are sold with three methods of corrosion control:

- Electrical isolation from pumps and other stray current sources
- Protective coatings as the primary means of corrosion control on the buried tank exterior
- Prepackaged galvanic anodes intended to prevent corrosion at coating holidays

Unfortunately, the cathodic protection systems are marketed with a misunderstanding of why different galvanic anodes are chosen. The STI website states:<sup>125</sup>

#### 5.0 ANODE INTEGRITY

5.1 STI-P3 tanks may be equipped with either zinc or magnesium anodes. Whereas magnesium anodes are designed only for installation in soil resistivities of 2000 ohms-cm or greater, zinc anodes are effective in all soil resistivities

Most managers, having no background in cathodic protection, will choose the zinc anodes based on the recommendation that they are “effective in all soil resistivities.”



**Figure 6.91** STI-P3 tanks in storage prior to installation.

This recommendation on the use of zinc anodes is the reverse of most recommendations on the use of zinc anodes. These tanks are not sold with anode backfills, so the natural resistivity of the local soil will determine the corrosion rate of the anodes, and zinc anodes cannot be effective in high-resistivity soils.

The lessons to be learned from this situation are:

- STI-P3 tanks are sold with inappropriate cathodic protection systems.
- What appears to be an industry standard may be a marketing organization recommendation.
- Industry standards and marketing organizations can contain mistakes.

Above-ground storage tanks have many advantages, including ease of inspection, for many oil and gas production operations.

#### Summary of Cathodic Protection

Cathodic protection is a widely used means of lowering corrosion rates. The early advocates of cathodic protection usually did not claim perfect protection, merely a reduction in leaks. While cathodic protection has lowered corrosion rates on oil and gas production structures for many years, it cannot stop all corrosion, and all cathodic protection systems must be periodically inspected to insure that they are working correctly.

#### Standards for Cathodic Protection

The list below shows some of the international standards relevant to cathodic protection. These are

consensus standards based on industrial practice at the time of publication and are reviewed and revised on a periodic basis. The current version of the standard should always be used. As one example, NACE SP 0169-2007 is the 2007 version of a standard that originated in 1969. Significant changes have been introduced into this and many other standards. While earlier versions of these standards are sometimes difficult to obtain, it is important to recognize that existing equipment and systems may reflect earlier versions of standard industrial practice. Earlier versions of these standards can be obtained from technical libraries and from the issuing organization. Most current standards can be downloaded from the Internet.

### ***NACE Standards***

- SP0169, Control of External Corrosion on Underground or Submerged Metallic Piping Systems
- SP0176, Corrosion Control of Submerged Areas of Permanently Installed Steel Offshore Structures Associated with Petroleum Production
- RP0177, Mitigation of Alternating Current and Lightning Effects on Metallic Structures and Corrosion Control Systems
- SP0186, Application of Cathodic Protection for External Surfaces of Steel Well Casings
- RP0193, External Cathodic Protection of On-Grade Carbon Steel Storage Tank Bottoms
- RP0286, Electrical Isolation of Cathodically Protected Pipelines"
- RP0285, Control of External Corrosion on Metallic Buried, Partially Buried, or Submerged Liquid Storage Systems
- RP0286, Electrical Isolation of Cathodically Protected Pipelines
- RP0388, Impressed Current Cathodic Protection of Internal Submerged Surfaces of Steel Water Tanks
- RP0675, Control of External Corrosion on Offshore Steel Pipelines
- TM 0497, Measurement Techniques Related to Criteria for Cathodic Protection on Underground or Submerged Metallic Piping Systems

### ***ASTM Standards***

- ASTM G 8, Cathodic Disbonding of Pipeline Coatings

- ASTM G 19, Cathodic Disbonding of Pipeline Coatings by Direct Soil Burial
- ASTM G 42, Standard Test Method for Cathodic Disbonding of Pipeline Coatings Subjected to Elevated Temperatures
- ASTM G 95 "Test Method for Cathodic Disbondment Test of Pipeline Coatings (Attached Cell Method)

### ***DNV Standards***

- DNV-RP-B401, Cathodic Protection Design
- DNV-RP-F103, Cathodic Protection of Submarine Pipelines by Galvanic Anodes

### ***British Standards***

- BS 7361-1, Cathodic Protection
- EN 12068, Cathodic Protection. External Organic Coatings for the Corrosion Protection of Buried or Immersed Steel Pipelines Used in Conjunction with Cathodic Protection. Tapes and Shrinkable Materials
- EN 12473, General Principles of Cathodic Protection in Seawater
- EN 12474, Cathodic Protection for Submarine Pipelines
- EN 12495, Cathodic Protection for Fixed Steel Offshore Structures
- EN 12499, Internal Cathodic Protection of Metallic Structures
- EN 12696, Cathodic Protection of Steel In Concrete
- EN 12954, Cathodic Protection of Buried or Immersed Metallic Structures. General Principles and Application for Pipelines
- EN 13173, Cathodic Protection for Steel Offshore Floating Structures
- EN 13174, Cathodic Protection for Harbour Installations
- EN 13509, Cathodic Protection Measurement Techniques
- EN 13636, Cathodic Protection of Buried Metallic Tanks and Related Piping
- EN 14505, Cathodic protection of complex structures
- EN 15112, External Cathodic Protection of Well Casing
- EN 50162, Protection against Corrosion by Stray Current from Direct Current Systems

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## INSPECTION, MONITORING, AND TESTING

The concepts of inspection, monitoring, and testing often overlap, and many organizations have slightly different definitions of the terms. For the purposes of this book, the following ideas will be used to differentiate between the various terms:

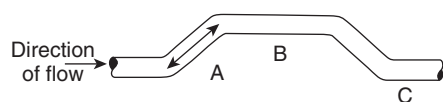
- Inspection is used to determine the condition of a system.
- Monitoring is used as a tool for assessing the need for corrosion control or the effectiveness thereof.
- Testing has two oilfield definitions. Hydrostatic testing involves filling a structure with liquid to determine if it has an adequate strength to withstand the desired stresses or pressures, which often involve code-mandated safety factors. Other tests are performed to determine the suitability of equipment, materials, chemicals, and so on for use in field applications. These tests are often performed in laboratories, but may also involve field trials.

The equipment involved in oilfield production is so large and complicated that inspections and monitoring procedures must be selected in a cost-effective manner to insure safe and efficient operation. It is important to recognize that not every process can be inspected, monitored, or tested before or during operation. The Pareto principle, often expressed as the idea that approximately 80% of all problems come from 20% of the equipment involved, or the concept of the “insignificant

many and the mighty few,” has been used by many organizations to prioritize inspection, monitoring, and testing.<sup>1–3</sup> In recent years, these concepts have been adapted to include formal risk-based inspection procedures.<sup>4</sup> At the time of this writing, the American Petroleum Institute (API) risk-based inspection standards have concentrated on downstream operations, but they also have been applied to production and pipeline operations for many years. The standard has guidelines for pressure vessels, heat exchangers, atmospheric storage tank shell courses and bottom plates, compressors, pumps, and pressure relief devices. All of this equipment is common to upstream as well as downstream operations, and the standard is divided into sections on inspection planning, determination of the probability of failure, and modeling consequences.<sup>5</sup>

Figure 7.1 shows a simple illustration of these ideas. The horizontal piping shown in Figure 7.1 has three areas of differing corrosion risks. Organizations are likely to concentrate both inspection and monitoring efforts in locations A and C of this structure because they are the locations where corrosion and/or erosion damage is more likely. Testing for the effectiveness of corrosion inhibitors should also emphasize the flow conditions in these areas, and it is likely that corrosion control efforts effective in these high-susceptibility locations will also be effective in low-susceptibility areas like location B in Figure 7.1.

Identification of these high-priority areas is the reason why design, operations, and inspection personnel need to understand the different kinds of corrosion and other degradation mechanisms likely to occur on specific types of equipment.



- A. Water oscillates—corrosion accelerated
- B. Corrosion not accelerated
- C. Water impinges at C—corrosion accelerated with higher flow rate (above limiting velocity).\*

\* Limiting velocity—velocity above which erosion damage can be expected.

**Figure 7.1** Areas of increased corrosion susceptibility in a horizontal piping system.<sup>6</sup>

## INSPECTION

Inspections can be planned and scheduled or occur during unplanned shutdowns, construction modifications, and so on. The primary purpose of inspections is to assess the fitness for intended service of the equipment in question. Most inspections are intended to be nondestructive, and industry tends to use the terms nondestructive testing (NDT), nondestructive inspection (NDI), and nondestructive evaluation (NDE) interchangeably.<sup>4</sup>

Fabrication-related NDT tends to emphasize welding, locations where manufacturing defects are more likely to occur, and in-service inspections also concentrate on welds, which tend to be locations more likely to be associated with structural failure, and on corrosion.

Choosing where to inspect depends on an understanding of the structural loading of the equipment concerned as well as the flow patterns of any fluids involved and any other parameters likely to affect long-term equipment reliability and corrosion degradation.

Risk-based inspection procedures are intended to concentrate efforts on high-risk, high-consequence (e.g., safety or expense) failure locations within in a system. Projected results of using risk-based inspection priorities are likely to result in increased inspection intervals for most inspection locations and some high-consequence locations where increased inspection frequency will be indicated. The purpose of these procedures is to move from mandated or calendar-based inspection to inspections based on logic, data, and documented experience.<sup>5</sup>

The following discussion covers some of the NDT inspection methods most likely to be used in upstream oilfield operations.

### Visual Inspection (VI)

The most common form of inspection is VI to identify surface abnormalities that can affect system perfor-



**Figure 7.2** The use of a manual pit gage to measure the depth of external pitting on a pipeline.

mance. Optical aides such as pit gages, borescopes, fiber-optic cameras, and TV-camera remote-operated underwater vehicles (ROVs) extend VI beyond locations where inspectors can have personal access.<sup>7</sup> Figure 7.2 shows a manual pit gage being used to measure the depth of pitting on the exterior surface of a pipeline.

Surface cleaning, not necessary with some other techniques, is very important for VI, especially when checking for cracks, for example, from stress corrosion or corrosion fatigue. Once marine growth was removed, the pit shown in Figure 5.21 was visible. Fracture mechanics analysis then determined that underwater welding was necessary to prevent this pit from becoming a dangerous stress riser that could lead to corrosion fatigue of the platform node.<sup>8</sup>

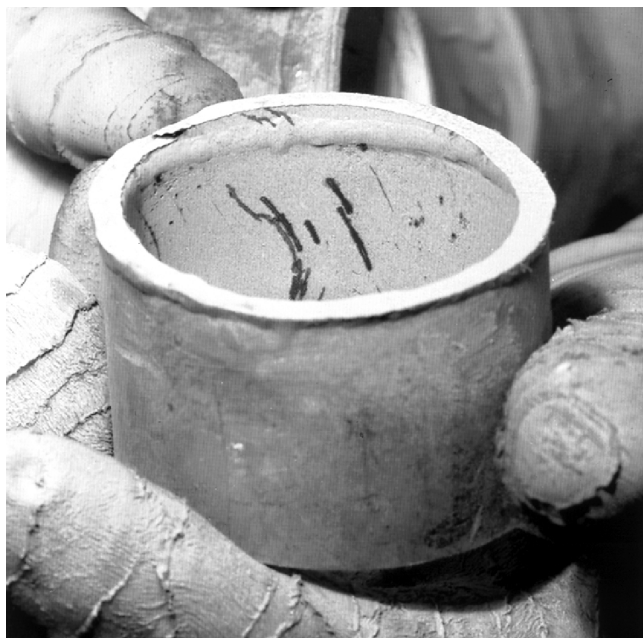
The primary advantage of VI is the curiosity and integrity of the individual inspector. While checklists and preplanned inspection procedures are important, this technique, more than others, allows the inspector to observe unanticipated phenomena. This is the reason why all inspectors need some training in all forms of degradation, mechanical and corrosion-related, that they are likely to encounter. Visual inspectors can also identify situations where other inspection techniques are appropriate.

Recent experience with pipeline corrosion has led to increased emphasis on VI, and external corrosion direct assessment and internal corrosion direct assessment techniques (including VI) have received increased emphasis in recent years.<sup>9-12</sup>

### Benefits of VI:<sup>4,7</sup>

- Large areas are quickly scanned
- Pit depths and pitting rates can be identified





**Figure 7.3** Dye penetrant indications of stress corrosion cracking on a stainless steel component.

- Video techniques can be used if personnel access is denied
- Does not require extensive training or equipment

#### **Limitations of VI:**<sup>4,7</sup>

- Internal inspection usually requires shutdown
- Borescopes and cameras only work during operation if medium is transparent
- Limited to surface defects

#### **Penetrant Testing (PT)**

PT, often called dye PT, can be applied to virtually any nonporous surface and is a common method of inspecting for cracks of all types. The procedure is fairly simple and inexpensive:

- The surface is cleaned.
- A high-surface-wetting liquid with a colored dye is applied to the surface and is allowed to seep into defects through capillary action.
- Excess penetrant is removed from the surface.
- A powdered developer is applied to pull the trapped penetrant from the defect and spread it on the surface so it can be seen.
- VI then determines the location of the defects.

Figure 7.3 shows dye penetrant indications of stress corrosion cracking on a stainless steel component.

Penetrants come in two basic types, fluorescent and visible penetrants, and are selected based on penetrating capability and contrast of the dyes. Fluorescent penetrants are primarily used in construction and manufacturing, and require the surfaces being inspected to be visually inspected using ultraviolet light. It is common for field inspectors to have portable aerosol cans of dye penetrant, cleaner/remover, and developer.

#### **Benefits of PT:**<sup>4,7,13</sup>

- Simple and rapid
- Makes surface defects easier to be seen
- Works on all nonporous materials

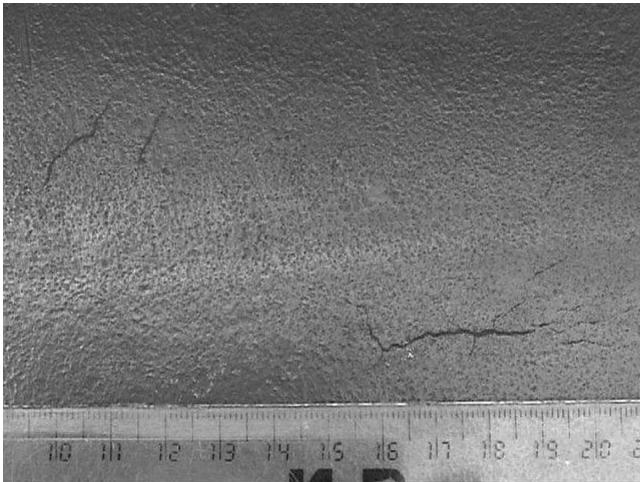
#### **Limitations of PT:**<sup>4,7,13</sup>

- Requires skilled inspectors
- Limited to surface defects
- Requires direct access to the surface being inspected
- Chemical cleaning and disposal is necessary
- Paint or coatings may mask defects

#### **Magnetic Particle Inspection (MT)**

MT serves most of the same purposes as dye PT, but it is considered to have two advantages. It can detect near-surface flaws (e.g., hydrogen blisters or weld defects) that would be missed by surface-specific inspection methods such as visual or dye penetrant inspection. For magnetic materials, it can sometimes detect smaller defects that would not be detected by penetrant inspection. It is used for detecting cracks and similar defects on welds, drill tools, pipelines, and any other iron-based or ferromagnetic components.

The process involves applying a magnetic field, either with permanent magnets or with an AC coil, to the area to be inspected. Then, a suspension of iron particles is sprayed onto the surface and the residual magnetic fields “decorate” surface or near-surface flaws—defects that interrupt the magnetic field in the magnetized part being inspected. It is common to apply these particles over a contrast-enhancing temporary coating and to use colored particles to enhance visibility. MT usually involves dry powder application of magnetic powders and visible light inspection, but wet sprays and ultraviolet light inspection is also possible.<sup>4</sup> MT can even be performed underwater to inspect subsea pipelines.<sup>1</sup> Figure 7.4 shows magnetic particle stress corrosion cracking indications on the exterior of an in-service crude oil pipeline.



**Figure 7.4** Magnetic particle crack indications on the exterior of a petroleum pipeline.

#### **Benefits of MT:**<sup>4</sup>

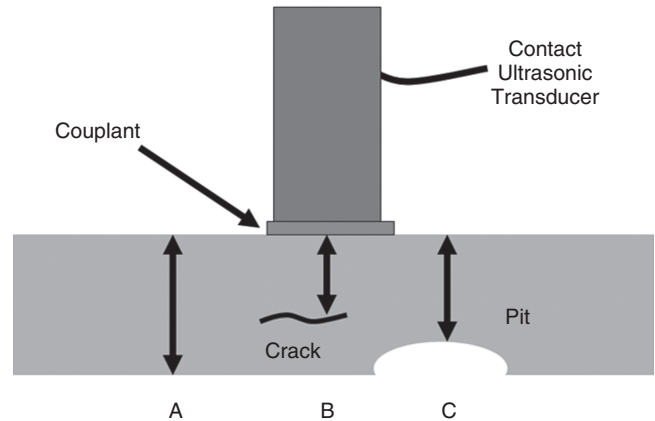
- Relatively simple and rapid method of inspection
- May detect fine cracks missed by eye and dye penetrant

#### **Limitations of MT:**<sup>4,14,15</sup>

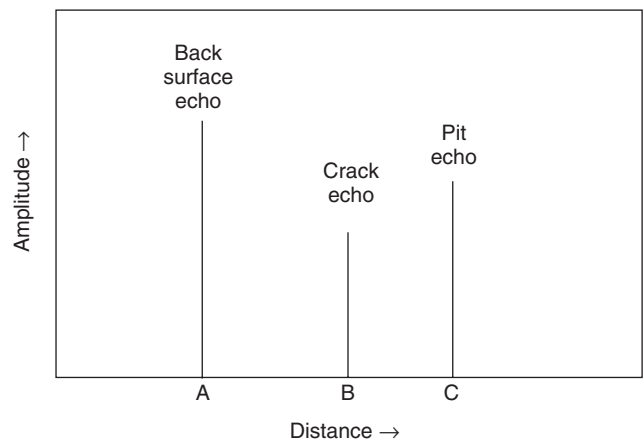
- Extensive training necessary
- Only ferromagnetic materials inspected
- Requires smooth, clean surface
- Paint or coatings may reduce sensitivity
- May need to demagnetize surface after inspection

#### **Ultrasonic Inspection (UT)**

UT uses high-frequency sound waves to measure the distance from a source transducer to a reflection source such as a defect or metal surface, for example, the opposite side of the metal being inspected. Any change in density of the material through which the sound wave is traveling will produce an echo which can be detected by ultrasonic detectors. This technique is usually used as a portable technique where the transducer (Figure 7.5) is placed on the metal surface to be inspected. The pulse (sending sound waves)-echo (receiving sound waves) technique is the most common UT technique.<sup>4</sup> High-frequency sound waves are introduced into a material (pulse), and reflected sound (echo) measurements indicate the distance from the material surface that the reflections (echoes) are coming from. Figures 7.5 and 7.6 show a typical setup where a transducer (sound source and receiver) is placed on the surface, and echoes from defects within the material and from



**Figure 7.5** Ultrasonic pulse-echo transducer with sample.<sup>4</sup>



**Figure 7.6** Pulse-echo display of the sample shown in Figure 7.5.<sup>4</sup>

the far side of the material produce three different return signals—the original pulse at the surface A, an echo from beyond the center of the sample B, and an echo from the far surface. The pulse-echo technique is used for determining remaining wall thicknesses due to corrosion and for weld flaw detection during construction and repairs.

It is common to monitor corrosion by inspecting in the same location at locations marked on the outside of pressure vessels and topside piping. Ultrasonics are also used for one-time inspections, as shown in Figure 7.7.

One limitation of conventional pulse-echo UTs is that they only indicate the condition of the structure at locations near the ultrasonic transducer. Other UT techniques have been developed to measure larger areas, although they are less commonly used.<sup>7</sup>

#### **Benefits of UT:**<sup>4</sup>

- Only requires direct access to one side of the test piece



**Figure 7.7** Ultrasonic inspection every meter at the 12 o'clock position on an exposed pipeline. Note the dark areas on the pipeline where dirt and debris have been removed so that good sensor contact can be maintained with the pipeline surface.

- Accurate thickness and flaw depth measurement
- Can penetrate thick materials
- Analytic techniques, based on ANSI/ASME B31G, API 653, API 510 and 510 and similar codes, can be used for determining maximum allowable operating pressures and estimated remaining service life.<sup>4,7,13,16–19</sup>

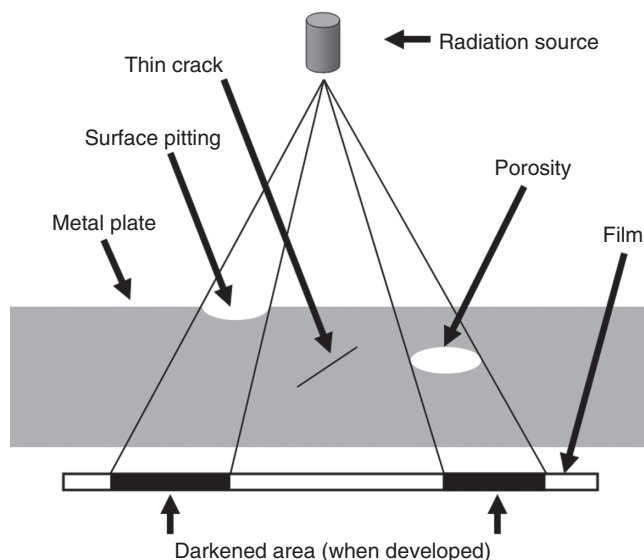
#### **Limitations of UT:**<sup>4</sup>

- Training is relatively extensive and may require several years of experience to produce skilled inspectors
- Limited use on very thin material

#### **Radiography (RT)**

The use of X-rays and gamma rays has been applied to industrial inspection for many years. The techniques are very similar to those used for medical radiography, and many advances in medical radiography have been adopted for industrial applications.<sup>4</sup>

Common oilfield uses for radiography include weld quality inspection, weight loss corrosion inspections, and the measurement of the extent of scale, hydrate, and paraffin buildup inside pipelines. A typical radiographic exposure using film as a radiation detector is shown in Figure 7.8. The radiation is absorbed by any material between the source and the detector. Figure 7.8 shows that thin cracks are normally missed by radiography, but volume defects, for example, pitting corrosion and internal porosity, are readily detected.



**Figure 7.8** Schematic of film radiography of a metal with a corrosion pit, an internal crack, and internal porosity defects.

Oilfield radiography uses X-ray generators, which require high-voltage electricity, or radioisotopic gamma rays. Isotopic radiation sources are limited in the radiation flux they can produce, and they often require longer exposure times than X-rays. A number of radioactive isotopes are available, but Iridium 192 is the most commonly used gamma source for oilfield use.<sup>20</sup>

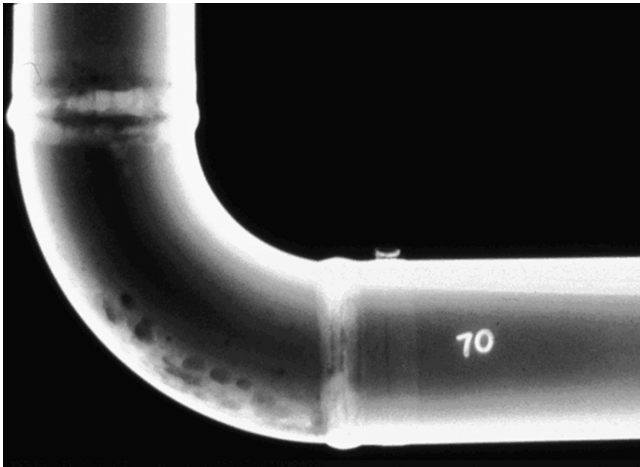
At one time, image capturing was with film, but recent advances in electronic radiation detection are capturing much of the market. These electronic methods use similar equipment, for example, image plates, but they can be processed much quicker, present no chemical disposal problems, and are more amenable to automated image transfer and analysis. These advances have led to significant cost and time reductions.<sup>20</sup>

Radiography detects differences in mass between the source and the imaging device. Heavier or thicker materials require longer exposure times, and lighter materials may not be detected. This can be an advantage, as radiography of coated pipelines does not require coating removal before examination. This is shown in Figure 7.9, which shows the effects of erosion corrosion on the inside of a coated pipe.

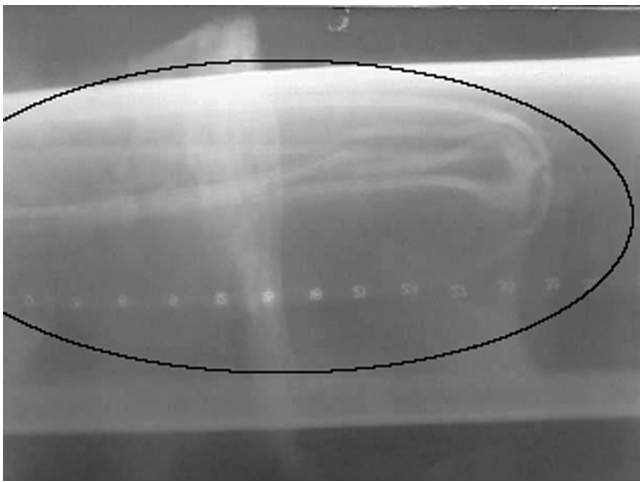
Radiography allows inspection and imaging of materials lighter than metals. This is shown in Figure 7.10, where a region of debonding has been located in a nonmetallic liner using radiography. A nearby flange showing the lining is shown in Figure 7.11. Despite this capability, the great majority of oilfield uses for radiography remain in weld quality and metal loss imaging.

Radiation safety is a major concern when using radiography, and dosage monitoring of all nearby personnel, exclusion of non-necessary personnel from





**Figure 7.9** Radiograph showing erosion corrosion at piping bend. Photo courtesy of NACE Basic Course.



**Figure 7.10** Radiograph showing damage to nonmetallic pipe liner.

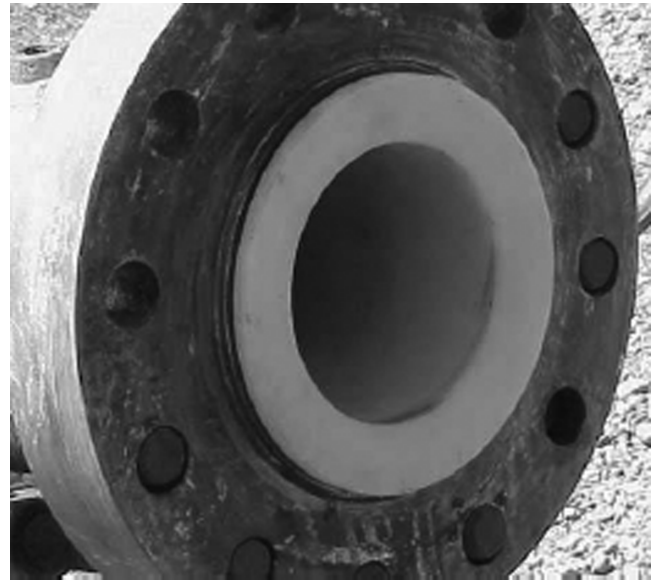
the exposure area, and appropriate radiation shielding are all necessary.

**Benefits of Radiographic Inspection:**<sup>1,4,7,20</sup>

- Rapid using electronic cameras instead of film
- Image as permanent record
- Coatings and thin surface deposits are transparent which allows minimal surface preparation
- Can be used on most materials
- Shows fabrication errors (e.g., misalignments), weld defects, and weight loss corrosion

**Limitations of Radiographic Inspection:**<sup>1,4,7,20</sup>

- Only local areas can be inspected
- Only 2D image—no information on depth of defect



**Figure 7.11** Flange near damage shown in Figure 7.10.

- Access to both sides of the structure is necessary
- Radiation safety precautions necessary
- Free access necessary for radiation source
- Orientation of crack-like defects means they may be missed
- Expensive

Because radiography cannot determine the depth of internal defects and will miss tight cracks like those shown in Figure 7.8, it is common to combine radiography with UT. The two techniques are considered complementary in locating and identifying internal defects.

**Eddy Current**

Eddy current inspection can be used on any electrically conductive material. Alternating electromagnetic fields induce circulating eddy currents (electron flow) in the material being inspected. Defects, for example, cracks, bulges, corrosion pits, alter the flow of these currents and reduce the secondary magnetic field of the part under inspection. Changes in conductivity and magnetic permeability are analyzed and correlated with flaws.

The basic equipment consists of an alternating electrical current source, a connected coil (probe) that can be passed near the part being inspected, and a voltmeter to measure the voltage change across the coil. The examination process involves moving the probe across the part being inspected and noting where the current changes. Figure 7.12 shows inspection of heat exchanger tubing. In this type of inspection it is common to draw the probe through the tubing and note locations where





**Figure 7.12** Eddy current inspection of heat exchanger tubes.<sup>3</sup>

indications appear. Further inspection, for example, with ultrasonics, can identify the extent of the irregularity detected by eddy current. Heat changer inspections can analyze many tubes very quickly. It is common to block off any tubes with eddy current irregularities until the total number of blocked tubes affects equipment performance.

#### ***Benefits of Eddy Current Inspection:***<sup>4</sup>

- Detects both surface and slight subsurface defects
- Probes do not have to contact the part
- Works through paint and some coatings

#### ***Limitations of Eddy Current Inspection:***<sup>4</sup>

- Relatively extensive training is required
- Limited to conductive materials
- Limited depth of penetration

#### **Positive Material Identification (PMI)**

This term is applied to identification and confirmation of alloy materials using hand-portable X-ray fluorescence (XRF) spectrometers.<sup>21</sup> A radiation probe, usually using a radioactive isotope, is placed on the sample in question and X-rays from the sample being tested are analyzed using equipment-mounted software. Most of these instruments can be programmed for dozens of alloys and the typical readout tells the operator the alloy with the closest match to the detected X-rays.



**Figure 7.13** Hand-held Thermo Scientific Niton X-ray fluorescent spectrometer being used for positive materials identification. Photo courtesy of Thermo Fisher Scientific.

Figure 7.13 shows one of these XRF analyzers in operation. All the operator needs to do is clean the surface so that the bare metal is exposed and turn on the detector. The machine will analyze the sample in a matter of seconds and compare it with a series of preloaded alloy possibilities before providing the nearest match.

Hand-held PMI detectors have become the industry standard for PMI of corrosion-resistant alloys (CRAs).<sup>21</sup> The portable X-ray spectrometers used for this purpose cannot detect carbon and other light elements, and hardness testing is the traditional way of sorting carbon steel samples.

***Benefit of PMI:***<sup>21</sup> Fast and accurate alloy identification

#### ***Limitations of PMI:***<sup>21</sup>

- Radioactive, requires secure storage and dosage monitoring
- Cannot analyze carbon steels and other light elements
- Requires direct access to cleaned surface for analysis
- Initial equipment cost is relatively high compared to some other techniques

#### **Thermography**

Thermography uses infrared cameras to detect temperature differences in equipment. It is often used as a remote inspection technique to determine fluid levels in storage tanks, fluid leaks on insulated piping, losses in wall thickness due to erosion corrosion, and a variety of



**Figure 7.14** Slumping storage tank due to wall thinning.

other purposes.<sup>7</sup> The technique cannot identify the reason for the detected temperature differences. It is used as a quick means of determining locations where closer inspection using other means are appropriate.

**Benefit of Thermography:**<sup>7</sup> Identification of hot spots, for example, due to scale buildup in furnaces or leaks in thermal insulation

**Limitation of Thermography:**<sup>7</sup> Cannot determine corrosion or wall thinning

### Additional Remarks about Inspection

There are a number of other inspection techniques used in oilfield applications, including magnetic flux leakage (MFL) for internal inspection of pipelines and alternating current field measurement (ACFM) for external crack detection.

Inspectors need guidance on how to collect and analyze, or protect for shipment for laboratory analysis, biological samples, and surface deposits.

One of the biggest problems with inspection is that it can become routine, and organizations may not pay attention to the results of inspection. This is shown in Figure 7.14, which shows an acid storage tank built from carbon steel that experienced gradual wall thinning due to corrosion. The use of carbon steel for the storage of concentrated sulfuric acid is an accepted industry practice.<sup>7,22,23</sup> This tank was inspected on a regular basis to determine the extent of the expected gradual wall thinning, and the original design called for replacement once the thinning reached a certain prescribed extent. Unfortunately, the inspection reports, which proved to be accurate, were filed and not brought to the attention of the appropriate decision makers. The tank was not

replaced at the appropriate time and a subsequent filling of the tank produced the slumping shown in this picture.

Upstream oil and gas operations have many routine inspections, but in far too many cases, the inspection process becomes routine, and organizations do not realize the implications of reports available somewhere in their organization. Preventable leaks and damaged equipment are sometimes the unfortunate results.

Many organizations would benefit from recognizing the Pareto principle that most problems are associated with a small fraction of their equipment.<sup>2,3</sup> Risk-based inspection procedures are attempts to apply this thinking.<sup>5</sup> Having more inspections is often counterproductive. Conducting the right inspections, in the most important high-risk locations, is preferable to having so many inspections that the organization spends too much time conducting inspections and too little time thinking about what these inspections mean in terms of safety and reliability.

Many organizations have maintenance and inspection budgets related to production volumes. As production fields age and production volumes decrease, equipment ages, and many production fluids become more corrosive. The need for increased inspection and maintenance suffers from decreasing budgets at times of increasing needs for inspection and maintenance.

## MONITORING

Inspection is used to determine the condition of equipment at the time of inspection while monitoring allows operators to determine if conditions and corrosion rates are changing. The two techniques are complementary, and both are necessary.

Corrosion monitoring is used to determine changes in the corrosivity of environments and to determine the effectiveness of corrosion control techniques such as chemical inhibitor injection.<sup>24</sup> Most oil fields become more corrosive as fields age, production rates decrease, and water cuts increase. Souring of formations, often caused by inadequate injection water treatment, can also cause increased corrosivity. In low-temperature, low-pressure situations where corrosion inhibitors are used to minimize and control corrosion rates of carbon steel, the proper application of corrosion monitoring becomes the principal means of determining and maintaining corrosion control.

### Monitoring Probes

Most monitoring techniques require the insertion of metal samples of some type into corrosive production

fluids. Two typical arrangements are shown in Figure 7.15. The corrosion coupon shown on the left is exposed to produced water at the bottom of the pipe and to oil which is flowing above the denser water. The flush-mounted probe on the right is only exposed to the produced water on the bottom of the pipe. It is obvious that the two different probes will be exposed to different corrosion environments and return different information.

It is important to monitor corrosion in the appropriate location. Common locations for internal corrosion are near the bottom or the top, depending on whether corrosion is expected from the water or the gas phase. Oil is generally noncorrosive.

A major limitation of monitoring systems is the limited size and shape of the probes used to monitor corrosion. Probes are manufactured from wire, sheet, or plate having chemistries close to, if not the same as, plate and tubular products used in oilfield applications. The crystal orientation and relative grain boundary areas of the exposed probe samples are different than the flat, as-rolled or as-drawn surfaces of most equip-

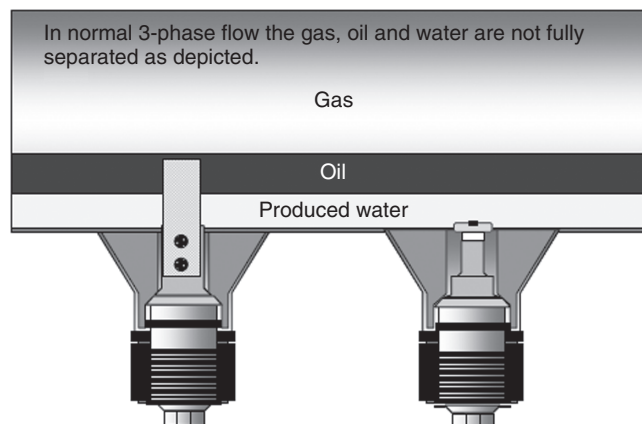
ment (Figure 7.16). For these reasons, most probes will have slightly higher corrosion susceptibilities than the actual structures in which they are placed. This produces slightly increased corrosion rates, which are conservative and are to be desired. The statistical nature of pitting and other forms of localized corrosion also mean that monitoring with small corrosion probes cannot replicate the corrosion rates of larger metallic structures. It is also difficult, and often impossible, to place probes in the most corrosion-susceptible locations in a complicated piping system.

While the true corrosion rates of large-scale equipment cannot be determined from small corrosion probes, “awareness of *changes* in the corrosion rate is often the major requirement of monitoring with the absolute value of the corrosion rate being less important.”<sup>4</sup>

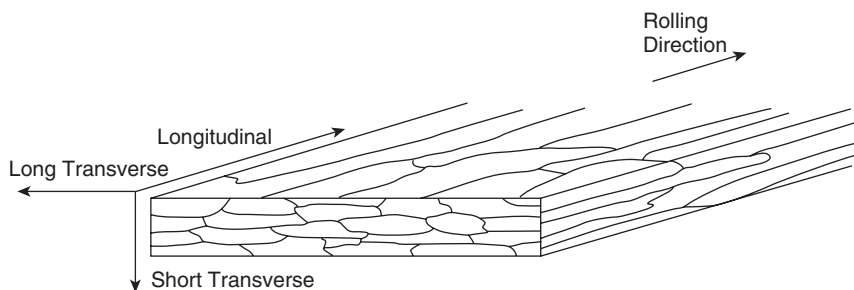
### Mass-Loss Coupons and Probes

The most common equipment used for corrosion monitoring is the insertion of mass-loss coupons into the environment of interest. Fittings such as those shown in Figure 7.16 are often used for this purpose. It is important that the coupons be inserted in the appropriate location, usually top or bottom depending on whether gas-phase or water-phase corrosion is being monitored. Unfortunately, it is all too common for the fittings and probes to be placed in the most convenient access location, and this means that many coupons are not exposed to the corrosive conditions they are intended to monitor. Figure 7.17 shows a typical weight loss coupon after exposure in an oilfield environment for 3 months. The arrows indicate locations of pitting.

NACE and other standards prescribe methods of analyzing coupons to determine the average (weight loss) corrosion rate and the pitting rate, based on the depth of the deepest pit on the coupon.<sup>6</sup> It should be noted that these methods calculate corrosion rates averaged over the exposure times and do not take into account the possibilities that the observed corrosion



**Figure 7.15** Intrusive and flush-mounted corrosion probes inserted into a three-phase production system.<sup>4</sup>

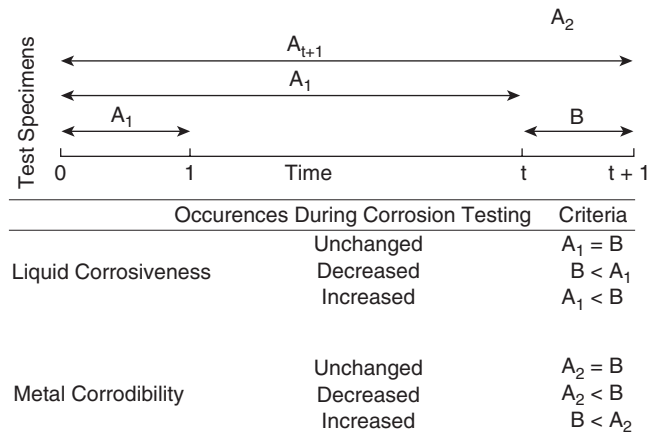


**Figure 7.16** Rolling direction and resulting grain structures.<sup>24</sup>





**Figure 7.17** A typical weight loss coupon after exposure to an oilfield environment for 3 months. Arrows indicate the three areas with pitting.



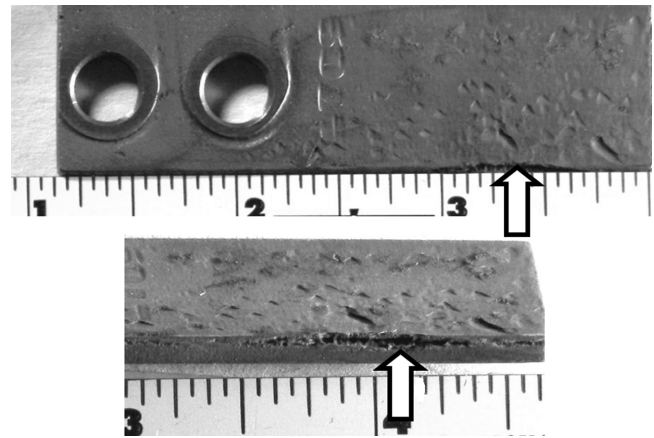
**Figure 7.18** Planned interval testing.<sup>25</sup>

may have occurred due to process upsets over a short interval of time during the exposure. This is a major limitation of the way most coupon exposure testing is conducted. Pitting initiation takes time, and there is no way of determining from mass-loss exposure coupons when, during the exposure interval, pitting, or any other form of corrosion, has occurred. The mass-loss corrosion rate also assumes that corrosion is general corrosion, which is seldom true for oilfield environments.

One means of determining if corrosivity has changed during the exposure interval is to use planned interval corrosion testing, a procedure that has been available since the 1940s. The principles of this method are shown in Figure 7.18. The method requires exposing numerous samples for different periods of time and comparing the corrosion rates for the various exposures.

This method, which has been available since the 1940s,<sup>26</sup> has been generally supplanted by online electrical corrosion monitoring techniques that can determine changes in corrosion rates in much shorter times. These techniques are discussed later in this chapter in the sections on monitoring and testing.

Corrosion coupons are normally supplied by companies that specialize in the preparation of these samples from standard alloys in accordance with Universal Numbering System (UNS) and similar alloy chemical-content standards. These alloys are similar to API-grade oil country tubular good (OCTG) alloys, but they are not the same. Differences in minor constituent chemis-



**Figure 7.19** Hydrogen-induced cracking on a carbon steel mass-loss coupon.

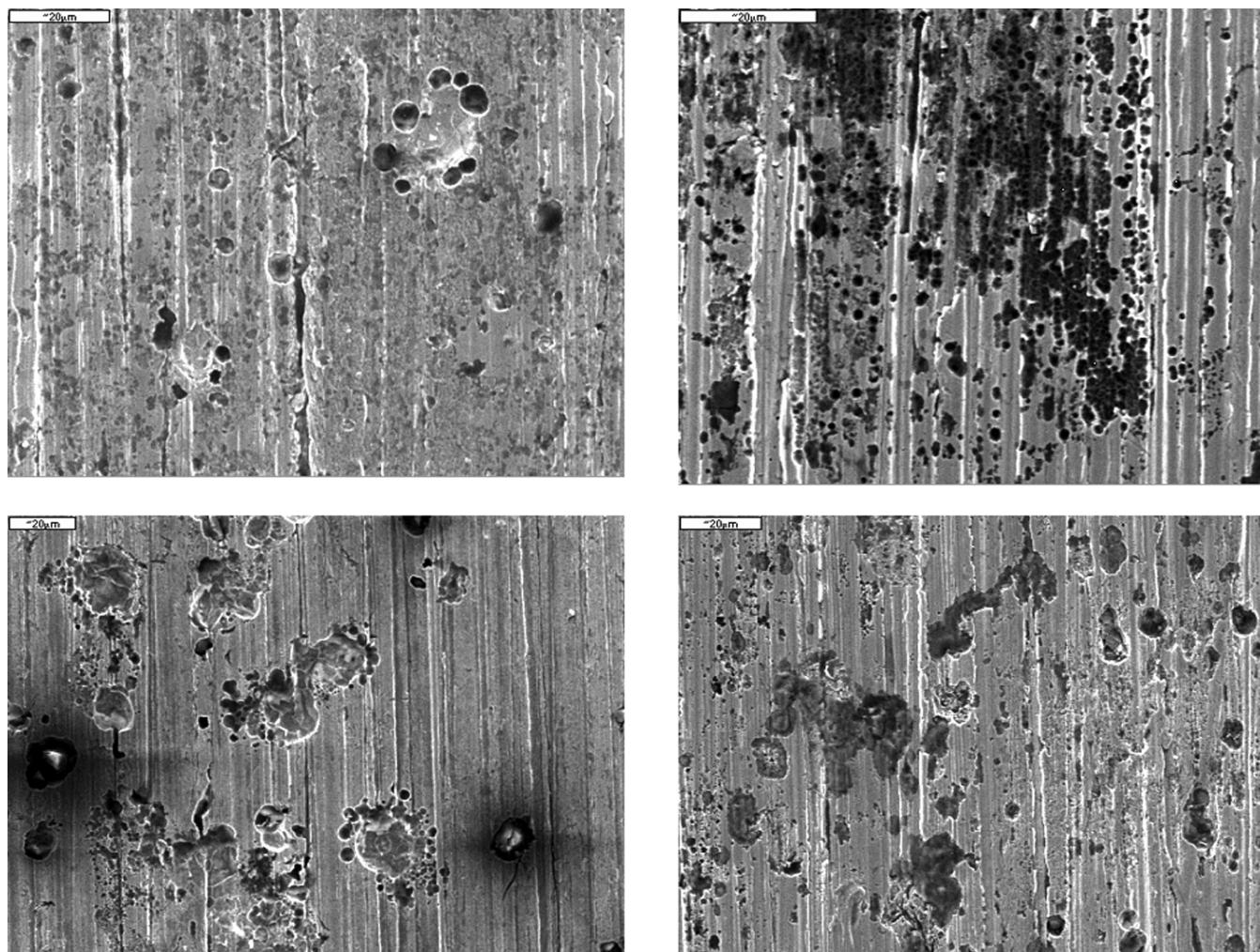
try, thermal and mechanical processing history, nature of inclusions and other imperfections, and so on, are likely in these coupons. These differences seldom affect the results of weight loss and pitting determinations, but they can produce unintended results in some environments. Figure 7.19 shows a typical carbon steel coupon purchased from a major coupon supplier and exposed in an  $H_2S$ -containing environment. The arrows show locations of hydrogen-induced cracking. The carbon steel in this coupon was harder (HRC27) than the OCTGs used in the equipment where the coupon was exposed. While the coupon had cracking, none is likely to occur on the piping system being monitored.

Coupon exposure time must be considered. Short-term exposures (15–45 days) are likely to indicate higher corrosion rates than longer-term exposures. It takes time for biofilms, scale deposits, and pitting to develop. Longer exposures (60–90 days) are sometimes necessary to detect and define pitting attack.<sup>25</sup> Pitting is normally analyzed using optical microscopes at relatively low magnifications. Figure 7.20 shows corrosion coupons from an offshore gas field analyzed using a scanning electron microscope. These instruments are able to observe surfaces at much higher magnifications and detect pitting that would be missed at lower magnifications.<sup>27</sup> This allows for faster corrections to corrosion inhibitor treatments. Many oilfield service companies have access to these microscopes, but the use of scanning electron microscopes for coupon analysis remains unusual.

#### **Benefits of Mass-Loss Coupons:**<sup>4,7</sup>

- Can be used in any corrosive environment
- Relatively simple procedure, easily understood, and widely accepted





**Figure 7.20** Scanning electron micrographs showing early indications of pitting on corrosion coupons from an offshore gas field.

- Works for general attack and localized corrosion mechanisms
- Mass-loss coupons are relatively inexpensive

- results of microbial or other films that produce underdeposit corrosion
- Labor-intensive technique

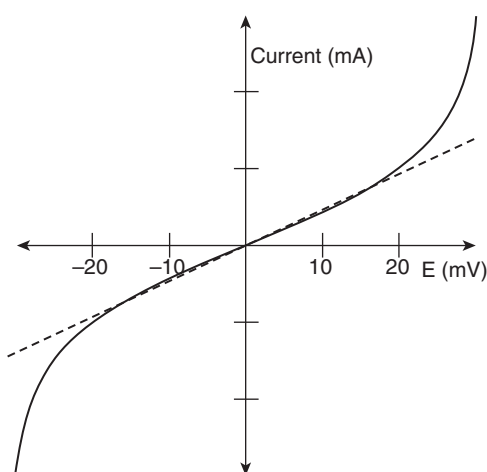
#### ***Limitations of Mass-Loss Coupons:***<sup>4,7</sup>

- Coupons must be inserted into the fluid, exposing personnel to potential hazards
- Practical limitations usually mean that data is only available 1–6 times per year
- Cannot be automated
- Only determines average corrosion rate, cannot determine effects of upsets or unusual occurrences
- Short exposure times overestimate general corrosion rates and may miss the onset of pitting or the

Mass-loss coupons are the most common means of monitoring the effectiveness of corrosion inhibitors for corrosion control. Unfortunately, many operators have the same contractor responsible for inhibitor application and for monitoring the effectiveness of the inhibitors. This conflict of interest can lead to problems. Another problem with mass-loss coupons is that it is often impossible to place them in the most corrosive locations. Organizations that rely on this data, instead of on inspections of the equipment involved, can experience unanticipated equipment failures. Coupons, like all



**Figure 7.21** Typical ER probes.<sup>4</sup>



**Figure 7.22** Voltage versus potential plot at potentials near the equilibrium (corrosion) potential.

other monitoring techniques, can only indicate whether the corrosion rates are changing. They cannot identify what the corrosion rates are on the most corroded equipment in a system, often in deadlegs, the bottom of upward inclines like shown in Figure 7.1, or other inaccessible locations.

### Electrical Resistance (ER) Probes

ER probes allow continuous online monitoring of corrosion and are the second most common monitoring technique for oilfield corrosion. Figure 7.21 shows typical commercially available ER probes. The probes are based on the principle that as corrosion or erosion of the probe occurs, the reduced metal has increased resistance to electrical current. Monitoring the changes in resistance provides an indication of the corrosion inside process equipment. Figure 7.22 shows a number of different geometries, including several flush-mounted probes that do not extend into the fluid and measure corrosion at the vessel wall level.

The output from ER probes can be transmitted to any desired location.

These probes will work in any environment, and that is a major advantage over other online monitoring tech-

niques. Depending on the corrosivity of the environment and the probe design, it is possible to note changes in corrosion rates.

The resistivity of metals changes with temperature. Modern ER probe systems have temperature compensation built into the probes, so this is no longer a problem. Electrical probes can be shorted by sulfide deposits, and this is a major limitation to ER probe use.<sup>4</sup>

Response times for ER probes depend on the corrosivity of the environment and the metal cross section of the probes. While thinner probes could be manufactured, their service life would be too short, making them impractical. At present, response times range from 0.5 to 1 day at very corrosive environments to 5 to 10 days at the lower end of typical corrosion rates.<sup>28</sup>

### Benefits of ER Probes:<sup>4,7,28</sup>

- Continuous online monitoring possible
- Can be used in almost any environment
- Useful in monitoring inhibitor persistence
- Sensitive to both corrosion and erosion

### Limitations of ER Probes:<sup>4,7</sup>

- Results are indicative of general corrosion or erosion, technique does not measure localized corrosion. Specialized probes can be designed to sense crevice corrosion.
- Probes require insertion into the corrosive fluid.
- Response time is slower (hours to days) than for other electrochemical monitoring techniques.
- Iron sulfide deposits can produce misleading results.
- Temperature compensation techniques are not sensitive to rapid temperature changes.

### Electrochemical Corrosion Rate Monitoring Techniques

Electrochemical corrosion monitoring techniques include:<sup>4,7,24</sup>

- Linear polarization resistance (LPR)
- Tafel extrapolation
- Galvanic monitoring
- Electrochemical noise
- AC impedance spectroscopy

The first three techniques are appropriate for use in oilfield monitoring applications. The latter two, while they have many laboratory and research-oriented advocates, cannot at the present time produce better results than LPR and Tafel extrapolation. They also require much more expensive, and delicate, instrumentation, and will not be discussed, even though they do appear in the corrosion literature and standards.

Most of these techniques are based on Faraday's law, which shows a direct relationship between electric current and the mass of metal lost or deposited in an electrochemical cell. The determination of corrosion rates also depends on knowledge of the valency (oxidation state) of the corrosion reactions.<sup>7</sup> Most instruments are factory calibrated based on the assumption that the corroding metal is iron or carbon steel and corrosion produces  $\text{Fe}^{+2}$  (instead of  $\text{Fe}^{+3}$ ) ions. This is a conservative approach and is appropriate for corrosion monitoring, where changes in corrosion rates are more important than the determination of the true corrosion rates.

**LPR** Linear polarization probes are sold with electrodes made from the material being monitored; in most cases this is carbon steel. The probes are small and can be inserted into the fluids of interest in the same manner as ER probes. The technique is based on the observation that at potentials very near ( $\pm 20$  mV) the corrosion potential, the voltage versus current plot is frequently linear. This is shown in Figure 7.22.

The polarization resistance,  $R_p$ , is the slope of the voltage versus current line near the corrosion potential.<sup>4</sup>

$$R_p = \frac{\Delta E}{\Delta I} \quad (\text{Eq. 7.1})$$

where:

$R_p$  = the polarization resistance,  $\Omega$  (ohms)

$\Delta E$  = the change in potential

$\Delta I$  = the change in current

The polarization resistance is then converted to a corrosion current using the Stern–Geary equation, Equation 7.2:<sup>4</sup>

$$I_{\text{corr}} = \frac{\beta}{R_p} \quad (\text{Eq. 7.2})$$

where:

$R_p$  = polarization resistance,  $\Omega$  (ohms)

$I_{\text{corr}}$  = corrosion current, amps

$\beta$  = the Stern–Geary constant

The Stern–Geary constant can be calculated from theoretical considerations or directly measured in separate experiments.<sup>4,29–33</sup> As a practical matter, most instrument suppliers sell their instruments calibrated based on the “average” Stern–Geary constant for iron and carbon steel and on the assumption that corrosion of iron produces  $\text{Fe}^{+2}$  ions (instead of  $\text{Fe}^{+3}$  ions). These assumptions are justified for monitoring purposes, because the purpose of electrochemical monitoring is to determine if the corrosion rate is changing or is remaining steady. The absolute corrosion rate is not determined, but that is not the purpose of monitoring.

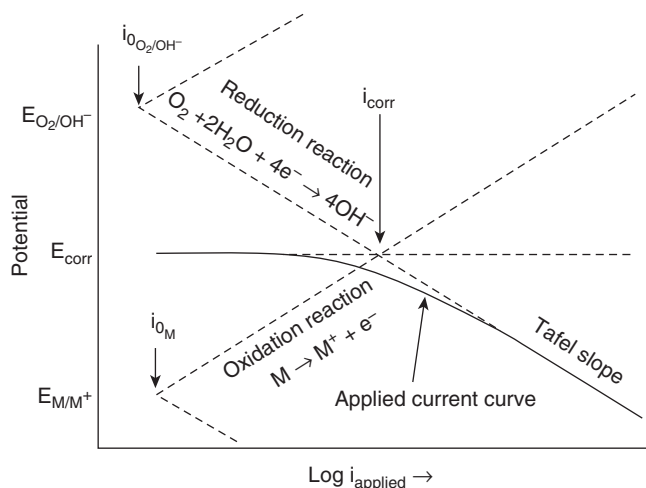
LPR instruments can determine changes in corrosion rates within minutes, sometimes even seconds. This real-time indication that corrosion rates are changing is the main advantage of this technique over the simpler and more widely used ER technique, which may take hours or days to respond to changes in corrosion conditions.

Like all electrochemical monitoring techniques, the electrodes must be kept free of fouling from oily deposits. This is a major limitation and is the reason why this technique is not more widely used in production monitoring before separation processes remove hydrocarbons from water.

**Tafel Extrapolation** This technique uses the same instrumentation as used in LPR monitoring, and most instruments are sold with the option of operating in either the LPR or the Tafel extrapolation mode. At potentials greater than a few millivolts from the equilibrium (corrosion) potential, potential-current plots frequently become linear on a log-linear plot when the potential is plotted on a linear basis and the current on a logarithmic scale. This is shown in Figure 7.23.

Prior to the application of applied current the voltmeter reads the corrosion potential relative to a reference electrode. As applied current is increased, the applied current versus potential curve shows no change in potential when most of the reduction current on the working electrode is due to the corrosion reaction. Eventually, the effects of the applied cathodic current become apparent and the curve slopes downward. Once most of the current is due to the applied current, the slope becomes linear and the original current becomes negligible. The log-linear portion of a polarization curve is called the “Tafel region,” in recognition of the





**Figure 7.23** Applied current cathodic polarization curve of a corroding metal showing Tafel extrapolation.

German chemist who first described this behavior. The Tafel slope is then extrapolated back to the original current to determine the oxidation (corrosion) current before added current was applied.<sup>33</sup>

This technique can measure low corrosion rates at equal or greater accuracy than weight loss measurements. It is possible to measure extremely low corrosion rates this way, provided that only one significant reduction reaction is involved over the potential range of the survey.<sup>33</sup>

**Galvanic Monitoring**<sup>34</sup> This very simple technique involves placing electrodes of two dissimilar metals (usually carbon steel and a more corrosion-resistant, therefore cathodic, metal) in the same electrolyte. A zero-resistance ammeter is installed to measure the galvanic current between the two electrodes. If the environment becomes more aggressive, the electrical current between the two electrodes changes and is an indication that something has changed to cause an increase in corrosion rates. It is used to monitor injection water piping systems, because the most common corrosion problem is air leaks or bacteria which depolarize the cathode and increase current flow between the two electrodes. The instrumentation for this technique is relatively simple and, like other electrochemical techniques, the results from many electrodes can be monitored at a central location.<sup>7,32</sup> The response time is as rapid as for LPR probes.

#### **Benefits of Electrochemical Monitoring Techniques:**<sup>4,7,31</sup>

- Faster response time than other techniques
- Real-time monitoring is possible

- Corrosion rate data can be obtained as often as measurements can be made
- Probes do not need to be removed to obtain data
- Probes can be remotely controlled to record and transmit data to a central location anywhere in the world
- Can provide information about the stability of a system such as the persistence of corrosion inhibitor films

#### **Limitations of Electrochemical Monitoring Techniques:**<sup>4,7,31</sup>

- Electrodes are subject to fouling by scale or bio-films; sulfide scales can also lead to erroneous results
- Probes require insertion into the fluid of interest
- Electrodes can become covered with oil or condensate, blocking off part of the electrode in multiphase systems
- Cannot measure localized corrosion
- Conductive sulfide deposits prevent use in sour systems
- Erosion cannot be measured

#### **Additional Comments on Electrochemical Monitoring**

Electrochemical monitoring has very fast response times, and some organizations have coupled electrochemical monitoring systems with automated control systems for corrosion inhibitor injection. This is not recommended for most oilfield situations because of the complicated interactions between corrosion inhibitors, scale, and hydrate inhibitors, and so on.

The LPR and Tafel extrapolation techniques should only be used in water systems after the majority of hydrocarbons have been removed. Galvanic monitoring is less sensitive and can work in multiphase systems, but it can only monitor corrosion in water-based liquid systems and will not monitor corrosion in top-of-the-line condensate locations.

Electrochemical monitoring instrumentation is often oversold. Many vendors claim that these techniques can be used for monitoring localized pitting and crevice corrosion and other phenomena. While this may be true in the laboratory, field use for identification and monitoring of pitting corrosion is not available and is unlikely considering the limitations of small electronic probe size compared to the large size of oilfield systems. These techniques are complementary to inspection techniques, but they cannot substitute for well-planned inspections.

Electrochemical noise and AC impedance spectroscopy are not suitable for use on oilfield corrosion moni-



toring situations with the single possible exception of using AC impedance spectroscopy to monitor coating systems for incipient breakdown in field tests of competitive coating systems.

### Hydrogen Probes

The reduction reaction associated with corrosion in acids and in sour service environments is hydrogen gas evolution. Some of the hydrogen atoms migrate into the metal and can cause hydrogen-induced cracking and

other problems. The use of hydrogen probe monitors is a relatively simple and inexpensive means of monitoring corrosion activity in these situations.<sup>7</sup>

There are three types of hydrogen probes:<sup>7</sup>

- Hydrogen pressure (or vacuum) probes
- Electrochemical hydrogen patch probes
- Hydrogen fuel cell probes

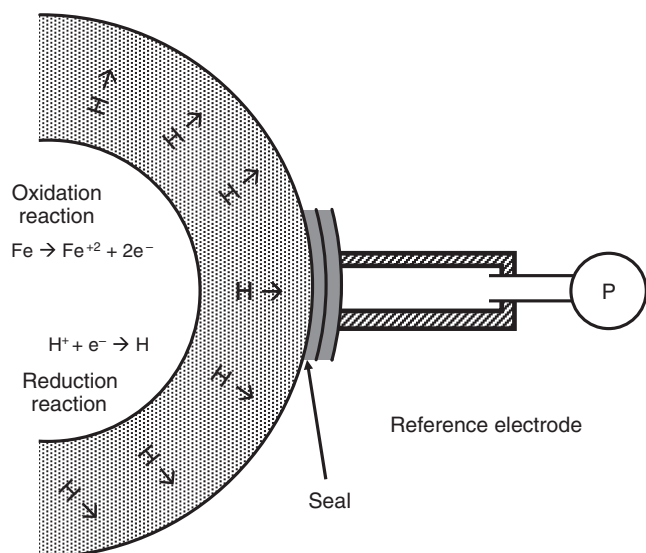
Figure 7.24 shows a schematic of a hydrogen pressure probe that can be externally mounted on the outside of pipelines or storage tanks. The seal between the probe and the structure must be gas tight, and this sometimes requires welded patches, although temporary probes that can be removed and used in other locations are also available. This type of probe can be used to monitor changes in corrosion activity due to internal corrosion inhibitor treatments. The results of one field study are shown in Figure 7.25.

Response times for hydrogen probes are typically several hours, and the probes can only sense corrosion activity for localized areas.<sup>35</sup>

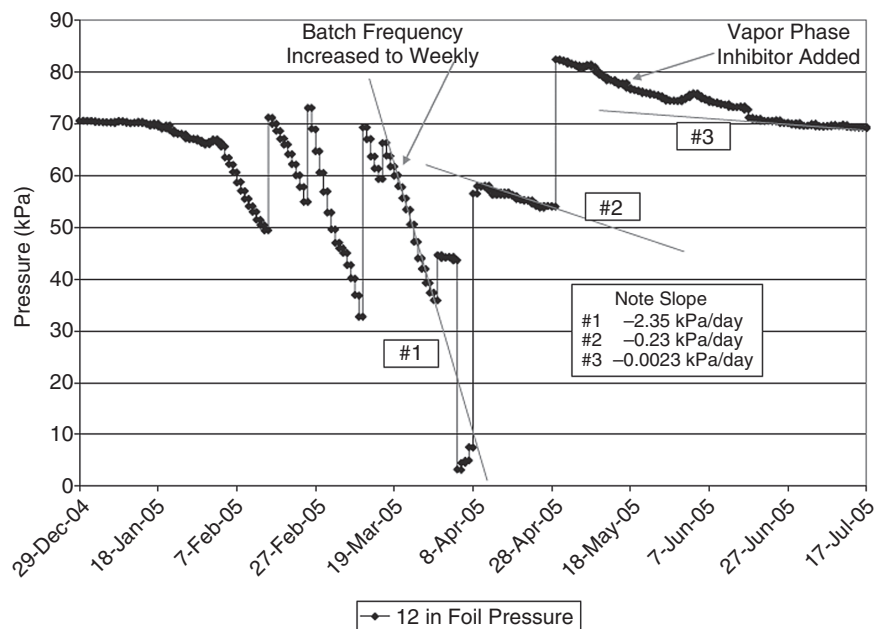
These probes have also been used to monitor hydrogen gas permeation into interior components of submerged offshore structures due to cathodic protection of the submerged exterior surfaces.

### Benefits of Hydrogen Probe Monitoring:<sup>7</sup>

- Useful to correlate with HIC and H blistering to warn of further events or increased damage



**Figure 7.24** Schematic of hydrogen pressure probe.



**Figure 7.25** Hydrogen probe monitoring of corrosion activity on inhibitor-treated pipeline.<sup>35</sup>

- Some hydrogen probes are easy to relocate to other areas of interest

#### **Limitations of Hydrogen Probe Monitoring:**<sup>7</sup>

- The correlation of hydrogen flux and corrosion varies, especially in situations where other chemicals can be involved in reduction reactions
- Not useful in oxygen reduction in neutral or base environments
- No accurate correlation between corrosion rates and hydrogen flux
- Welded patch probes may require stress relief
- Nonwelded patch probes are difficult to keep sealed to hydrogen and limited to the maximum temperature capacity of the seals

#### **Sand Monitoring**

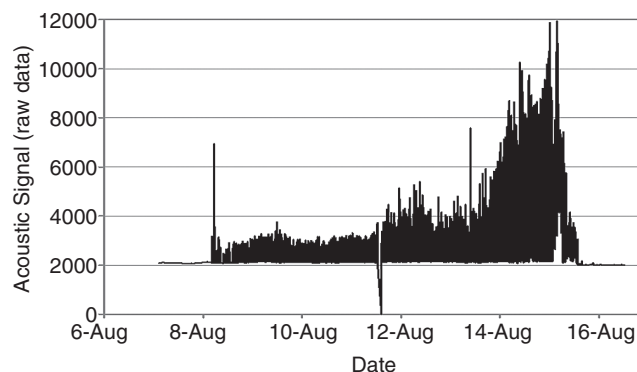
Sand monitoring is necessary for a number of reasons, including prevention of unexpected erosion failures on pipelines, wells, and topside piping systems.<sup>36</sup>

There are three major types of sand-monitoring probes. One form is an ER probe, as described above. The probes are usually made of a CRA, and as the probes wear away, the resistance increases. This technique is simple and reliable. The probe must be located in an appropriate area where erosion is to be expected to occur.<sup>1</sup>

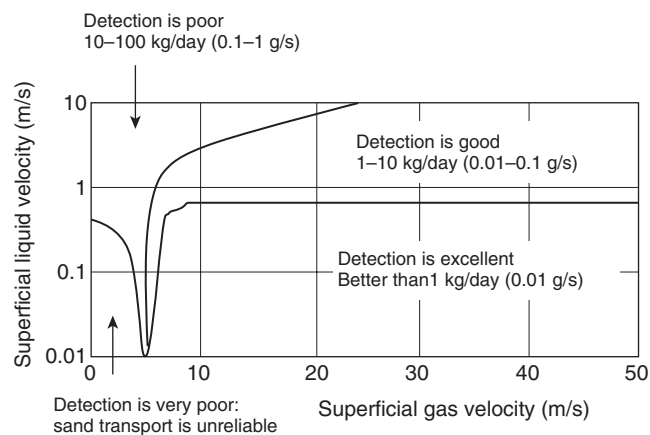
Another probe design involves a CRA tube with a vacuum. If the tube wears to the point that a leak develops, the vacuum is lost and an electric signal is generated. Once again, this technique is simple and reliable.<sup>1</sup>

Acoustic sand monitors are also available. These monitors can be mounted externally on piping, and the signal from them provides an indication of the volume of sand moving through the piping. An alternative version of this design involves inserting a probe into the fluid stream and monitoring the acoustic signal from the sand striking a sensing element. This system has the advantage of providing real-time data and warnings of when problems may develop. Figure 7.26 shows how the acoustic signal on a topside monitoring station indicated when a sand event (a large “slug” of sand) due to a gravel pack failure caused problems on an offshore platform.

The efficiency of acoustic sensors depends on the relative velocity of the fluids involved. Figure 7.27 shows a sensitivity regime map for a commercial acoustic sand detector. Detection is much more efficient in low-liquid fluid streams provided the superficial gas velocity is high enough (approximately 10 m/s [40 ft/s or more]).



**Figure 7.26** Acoustic data indicating the progressive sand production due to a gravel pack failure.



**Figure 7.27** Sensitivity regime map for a commercial acoustic sand detector.

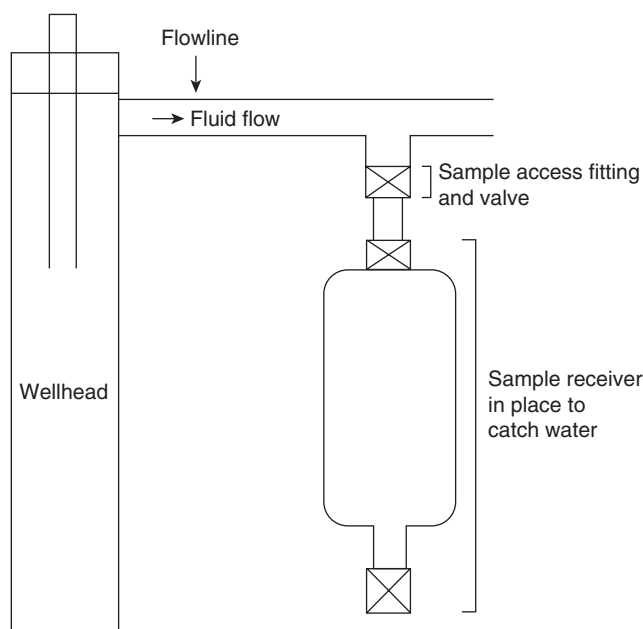
Location of sand sensors is critical. The best places are in locations where erosion is likely to occur, either immediately downstream from piping bends or from flow restrictions like valves or chokes.<sup>37</sup>

Whenever sand production is encountered, the presence and proper disposal of naturally occurring radioactive materials (NORM) must also be considered. These materials must be disposed of in accordance with local regulations for hazardous waste disposal.

#### **Fluid Analysis**

The chemical and suspended solid contents of production fluids can be monitored to analyze corrosion problems upstream of the sampling point. Chemical monitoring is also used to insure that treated fluids, for example, steam and injection water, do not cause corrosion, biological growth, or scaling problems.

**Sampling Procedures** Fluid sampling affects the validity of any chemical monitoring system. Various test probes and sampling ports can be placed in topside piping systems to monitor a variety of parameters.



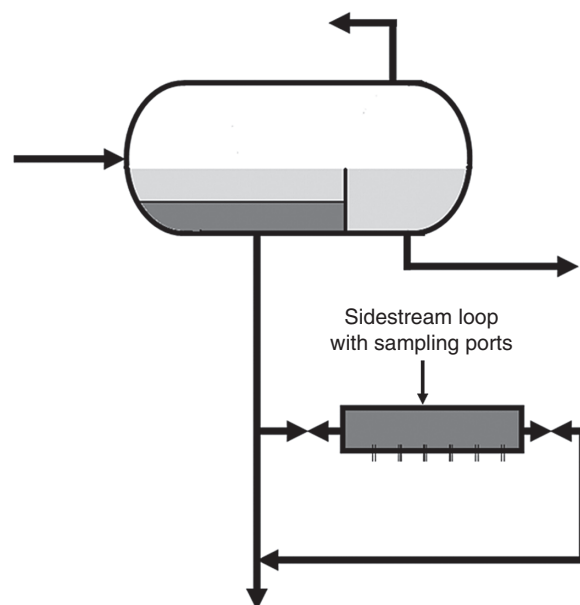
**Figure 7.28** Sample receiver for collecting water samples.<sup>38</sup>

Figure 7.28 shows a typical sampling receiver for collecting water samples for further analysis. These receivers are usually located below a flowline or similar piping system, but horizontal collection locations are sometimes used to avoid the collection of sand, silt, or micro-biologically created material.<sup>38</sup>

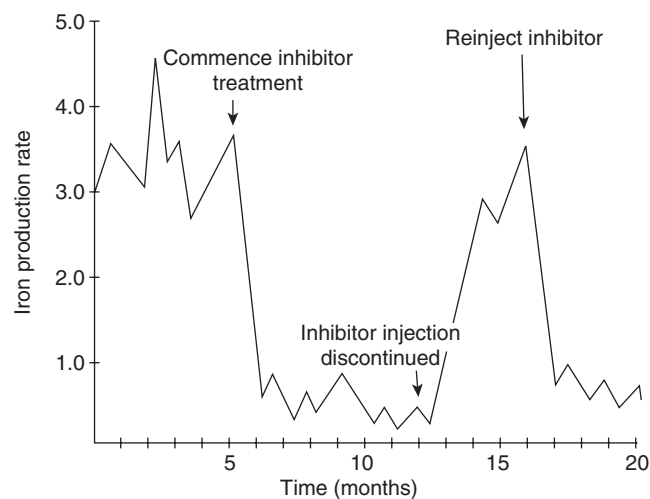
Multiple sensors can be placed in sidestream devices like the one shown in Figure 7.29. These sidestream devices should be located after oil-water separators to avoid hydrocarbon fouling of probes, coupons, and sensors. Devices like this have been used in power plants since the 1920s and are commercially available for use in both high- and low-pressure models for use in oil and gas production. Sidestream devices have the limitation that they do not reproduce the fluid flow patterns of the main flow channels, so they should only be used for sampling and monitoring those fluid parameters that will not be affected by diversion into the device (e.g., water chemistry).<sup>39</sup>

**Iron Counts** This corrosion monitoring technique dates back to the 1950s and is still widely used to provide a simple indication of corrosion activity upstream of the sampling point. Figure 7.30 shows the response of iron counts to corrosion inhibitor injection into a system.

NACE SP0192 contains detailed information on water collection and analytical procedures. The samples can be analyzed in the field using a variety of commercially available colorimetric tests or shipped to a laboratory. Iron count analysis needs to distinguish between iron associated with corrosion and naturally occurring



**Figure 7.29** Schematic of sidestream sampling device for drawing water samples or for continuous monitoring of water quality.



**Figure 7.30** Iron count rate history showing the effects of corrosion inhibitor injection.<sup>38</sup>

iron present in the formation water. A common way of doing this is to compare the iron content of the water sample with the manganese content. All carbon steel contains some manganese, and the manganese counts are typically from 0.5% to 1.5% of the iron counts.<sup>38</sup>

The lack of iron in produced water is not a guarantee of a lack of corrosion. Iron scale formation upstream of the sampling point is possible, especially in waters with neutral or higher pH and high carbonate contents. Manganese counts greater than approximately 1% of

the iron counts are a possible indication of iron scale formation.

**Benefits of Iron Counts:**<sup>7</sup> Quick, inexpensive, and easy field analysis

**Limitations of Iron Counts:**<sup>7</sup>

- Assumption is made that corrosion is proportional to iron content, but upstream mineral deposits may lower the iron counts
- Representative sampling may be difficult due to complicated flow conditions
- Not reliable in sulfide-containing systems

**Other Chemical Analyses Related to Corrosion Monitoring** Relatively clean water, for example, boiler feedwater, is often monitored for pH, electrical conductivity, and dissolved oxygen.<sup>7</sup> These measurements are usually conducted using commercially available probes. The probes are often mounted, along with ER or LPR probes, in sidestream sampling loops like shown in Figure 7.29, and online monitoring relayed to central control stations is common.

pH measurements provide direct evidence of changes in fluid parameters that affect corrosion. Low pHs are corrosive to carbon steel while neutral or higher pHs are relatively benign, especially in the absence of dissolved oxygen.

**Benefits of pH Monitoring:**<sup>7</sup>

- Simple
- Probes have rapid response

**Limitations of pH Monitoring:**<sup>7</sup>

- Interference from sodium, lithium, and potassium ions
- Frequent probe maintenance is necessary

The electrical conductivity of water is a direct measurement of the presence or absence of dissolved ions. Conductivity measurements are routinely used to monitor steam condensate systems. Any increases in conductivity are evidence of leaks into the system. These leaks are often from condensers, and it is common to monitor the pH immediately downstream from condensers. Many gas fields produce low-conductivity condensate, and conductivity monitors can also be used to monitor changes from the production of condensate and the onset of high-conductivity (high salt) formation water.

**Benefits of Conductivity Monitoring:**<sup>7</sup>

- Simple and rapid response
- Early warning of leak, for example, in steam or condensate return system

**Limitations of Conductivity Monitoring:**<sup>7</sup>

- Routine cleaning necessary to avoid bridging the electrodes
- Temperature sensitive

Oxygen is the most corrosive gas commonly found in topside oilfield fluids. The presence of dissolved oxygen is an indication of leaks into production fluids, which normally have very low oxygen concentrations. Oxygen scavengers can remove oxygen down to 1 ppb or less, although some boiler water treatments deliberately keep oxygen levels at 0.02 to 0.2 ppm in order to provide enough dissolved oxygen to passivate piping systems. Online oxygen probes are commonly used to monitor dissolved oxygen in topside production water and injection water systems. The presence of high levels of oxygen is an indication of leaks in the system and an indicator of the need for additional oxygen scavengers or other oxygen-control procedures. Electronic oxygen probes must be periodically replenished of the chemicals used to detect oxygen.<sup>7</sup>

**Benefit of Oxygen Monitoring:**<sup>7</sup> Changes in oxygen indicate problems in the system

**Limitations of Oxygen Monitoring:**<sup>7</sup>

- Electrode poisoning in hydrocarbon processes
- Other dissolved gases (H<sub>2</sub> and CO<sub>2</sub>) can interfere with measurements
- Regular maintenance of electrodes

### **Bacterial Growth Monitoring**

Microbially influenced corrosion (MIC) can occur on the exteriors of tank bottoms and on exteriors of buried or submerged piping. The presence of bacteria in these situations is unavoidable. Corrosion control by a combination of protective coatings and cathodic protection effectively minimizes this problem, and microbial growth monitoring is not necessary.

On the insides of piping systems, monitoring for the presence and growth of bacteria has been proven necessary in many circumstances. NACE TM0194 and other industry standards address this problem by suggesting methods for monitoring bacterial and the effectiveness



of biocide treatments.<sup>40</sup> The standard provides guidance on effective sampling and culture procedures for both planktonic, freely floating, and sessile, surface-attached, bacteria. A number of commercially available field testing technologies are available to determine bacterial populations and activity.

Planktonic bacteria, bacteria freely floating in the liquid, are collected using sampling devices similar to those shown in Figures 7.28 and 7.29. It is important that any liquid samples be contained in clean glass or plastic containers. Samples should be analyzed as soon as possible and, if delays of more than 1 h are unavoidable, the samples should be kept in air-tight glass containers. Refrigeration of samples kept for more than 4 h is also recommended.

Sessile bacteria grow in biofilms on metal surfaces. The standard discusses coupons for collecting these biofilms, often at the 6 o'clock position in oil and gas piping.

Sampling is recommended just prior to and after biocide treatments. Bacteria can then be cultured and assessed for responses to biocides.

### **Additional Comments on Monitoring**

Additional monitoring methods such as the field signature method for monitoring corrosion rates on subsea pipelines and topside piping are available and discussed in NACE and other publications.<sup>40</sup>

The purpose of monitoring is to identify when changes in corrosion rates are occurring and to correlate these changes with corrosion control procedures.<sup>4</sup> No monitoring method can identify actual corrosion rates. Oilfield systems are too complicated, the sizes of samples used to monitor corrosion are much smaller than the surface areas of exposed equipment and piping, and the metallurgical conditions of probe materials are different from the conditions on complicated structures which have welds, stresses, and other complications not replicated in monitoring samples. Once changes in corrosion rates are noted, causes and corrective action can be identified, for example, the need for additional corrosion inhibitors or changes in the corrosivity of produced fluids or injection water. Corrective actions can then be taken if necessary.

Many organizations suffer from too much monitoring. It is common to have chemical and inhibitor suppliers responsible for the application of the appropriate chemicals and also for the application and analysis of monitoring coupons or probes used to determine the effectiveness of these treatments. Aside from the obvious conflicts of having suppliers monitor their effectiveness, it is often the case that too many coupons or other sources of data are collected. This has been known to lead to organizations spending too much time

and effort on the insertion, removal, and collection of field monitoring data and not enough time analyzing the meaning of the data collected. Widely publicized oilfield failures have been associated with systems where hundreds of thousands of coupons had been collected, yet unexpected leaks on major equipment still occurred. The unfortunate consequences of reduced production rates are that oil fields become more corrosive at the same time that aging equipment and increased corrosivity require more corrosion control and monitoring.

Monitoring cannot replace inspection. The two procedures are complementary. Appropriate corrosion monitoring can reduce the need for inspections and indicate potential locations where problems are occurring and additional inspections are warranted.

## **TESTING**

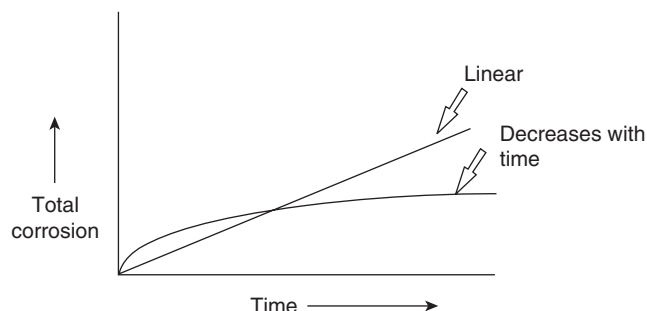
Testing is used in two senses in oilfield applications. Hydrostatic testing is commonly used to "proof" newly constructed or altered equipment to insure that the equipment will be safe to operate under the intended temperature and pressure conditions. The other use of the term is for relatively short-term laboratory or field trials to determine materials compatibility, the effectiveness or corrosion inhibitors, and so on.

### **Hydrostatic Testing**

Hydrostatic testing is required on pipelines and storage tanks after construction and major repairs. Incomplete removal of the hydrotest water after pipeline testing can result in major corrosion problems. While it would be desirable to use clean water for these tests, as a practical matter, river water or seawater is often used. If this water is not removed and the pipeline dried, then microbial colonies can form and corrosion can be noted in a matter of days. Treatment of the test water with biocides can minimize this problem, but disposal of the biocide-containing test water can become a problem. Industry standards on the treatment and disposal of hydrotest water are available.<sup>41</sup>

### **Laboratory and Field Trial Testing**

Laboratory and field trial testing procedures have been developed to provide short-term evaluation methods for new or replacement materials or chemical treatments prior to their adoption for field use. The tests tend to concentrate on potential weaknesses or vulnerabilities of the materials being tested, for example, H<sub>2</sub>S compatibility for metals and decompression resistance of polymeric liners.



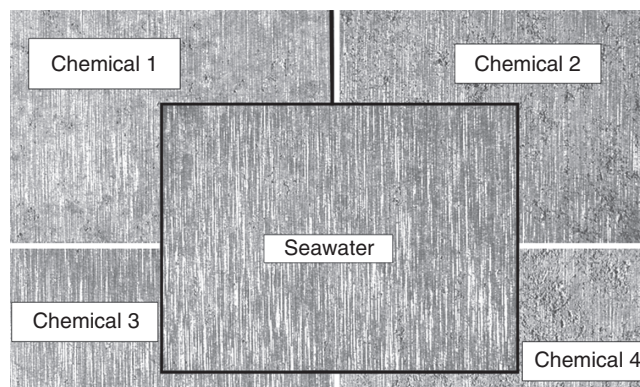
**Figure 7.31** Corrosion rate changes versus time.

**Test Duration** Accelerated laboratory tests rely on one of two approaches to produce short-term accelerated results. Either the environment is made more aggressive or the methods of determining incipient failure are improved over field conditions. Common means of making environments more aggressive include increasing temperatures, pressures, or concentrations of aggressive chemicals. Figure 3.6 showed how varying salt concentrations altered the corrosivity of brines by reducing the oxygen solubility. These interactive effects must always be kept in mind whenever developing corrosion testing protocols.

Testing and sampling evaluations need to recognize the time dependence of various kinds of corrosion. Most exposure testing involves weight loss measurements or electrochemical monitoring of corrosion rates. Figure 7.31 shows two idealized corrosion rate plots. The linear corrosion rate would be expected in acid environments where the corrosion is dependent on transport of reducible chemicals to the metal surface. This is relatively rare in oilfield applications. The parabolic, decreasing with time, kinetics are far more common. Exposures for very short periods would predict very high corrosion rates, whereas longer test exposures might reveal minimal increases in overall corrosion rates after the system equilibrates.

Reporting corrosion rates based on the weight loss or pitting depth after one time interval does not recognize the variations in corrosion rate shown in Figure 7.32 and identified by the planned-interval corrosion-testing procedure. Extrapolation of short-term tests is unlikely to predict the long-term corrosion rates of actual equipment. This is one reason why the planned-interval corrosion rate testing outlined in Figure 7.19 should be considered whenever developing exposure tests.<sup>25</sup>

Actual corrosion rates are relatively unimportant in laboratory screening testing. It is more likely that the testing will allow ranking of materials, chemical treatments, and so on by the order of corrosion resistance,



**Figure 7.32** High-magnification scanning electron microscope images of pitting corrosion.

and this will allow choices of materials or chemicals for further field tests.

**Laboratory Test Environments** There are at least eight different types of environments in which oilfield materials might be tested:<sup>42-44</sup>

- Sour water environments
- Sweet water environments
- HCl environments (associated with acidizing treatments of formations or scale removal from down-hole components)
- Drilling mud acid environments
- Organic acid environments
- Hydrocarbon environments
- Supercritical CO<sub>2</sub> environments
- Atmospheric environments of various types (e.g., marine, desert sunlight)
- Synthetic seawater

Materials compatibility should be tested in environments as close to the actual operating environment as possible, but this is not always possible. Standardized screening environments are contained in some standards. Tables 7.1 and 7.2 show two sets of these suggested environments.

Notice the high pressures and temperatures in Tables 7.1 and 7.2. This type of testing requires specialized high-pressure test chambers, called autoclaves, which are typically limited to several liters capacity. Laboratory testing under these conditions requires specialized equipment, and many service companies are available to do this kind of testing on a contract basis.

**Analysis of Samples after Exposure** Postexposure analysis of metal samples usually involves weight loss

**TABLE 7.1 Recommended Hydrochloric Acid Environments for Testing Materials Compatibility<sup>42</sup>**

A—Concentrated Acid	B—Partially Spent Concentrated Acid	C—Partially Spent Dilute Acid
15Twt % HCl	15Twt % HCl	1.5Twt % HCl
100Tmol % N <sub>2</sub>	16.5Tg/L CaCO <sub>3</sub>	1.65Tg/L CaCO <sub>3</sub>
80TH ± TH3°C (175TH ± TH5°F)	100Tmol % N <sub>2</sub>	100Tmol % N <sub>2</sub>
7.0TH ± TH0.3TMPa	80TH ± TH3°C (175TH ± TH5°F)	80TH ± TH3°C (175TH ± TH5°F)
(1000TH ± TH50Tpsig)	7.0TH ± TH0.3TMPa	7.0TH ± TH0.3TMPa
total pressure	(1000TH ± TH50Tpsig)	(1000TH ± TH50Tpsig)
	total pressure	total pressure

Source: Table 3, HCl Environments in Reference 42.<sup>42</sup>

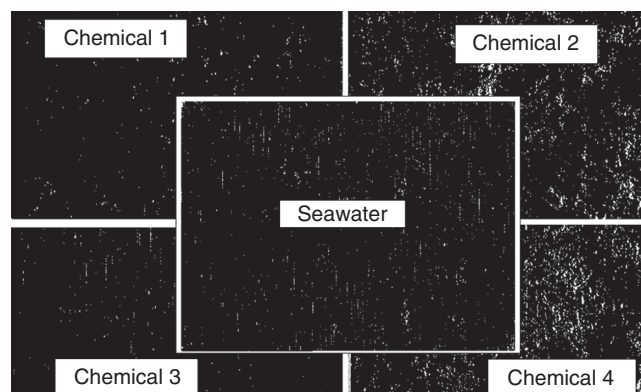
**TABLE 7.2 Suggested Sour Water Environments for Testing Materials Compatibility<sup>42</sup>**

A—High Temperature	B—Low Temperature
30Tg/L NaCl	30Tg/L NaCl
1Tmol % H <sub>2</sub> S	1Tmol % H <sub>2</sub> S
14Tmol % CO <sub>2</sub>	14Tmol % CO <sub>2</sub>
balance CH <sub>4</sub>	balance CH <sub>4</sub>
80TH ± TH3°C	50TH ± TH3°C
(175TH ± TH5°F)	(120TH ± TH5°F)
7.0TH ± TH0.3TMPa	7.0TH ± TH0.3TMPa
(1000TH ± TH50Tpsig)	(1000TH ± TH50Tpsig)
total pressure	total pressure

Source: Table 1, Sour Water Environments.<sup>42</sup>

determinations and low-magnification inspection for signs of pitting or crevice corrosion. The incubation times for these forms of corrosion may be longer than the laboratory test exposures. One means of compensating for relatively short exposure times is by examining the samples with high-powered microscopes which may detect pitting at levels not discernible to ordinary visual examination. The laboratory use of scanning electron microscopes has become routine for this purpose. These instruments are usually combined with X-ray spectrometers for chemical analysis, similar to those described in the section on positive metal analysis. The combination of high magnifications with chemical analysis of local areas is a major advantage of the use of scanning electron microscopes for laboratory and field failure analysis.

The pitting corrosion coupons shown in Figure 7.21 were from an offshore gas field. It is relatively easy to identify which of these coupons had the most corrosion. Laboratory screening tests, where exposure times are often limited, may require analysis and comparison of samples having less apparent corrosion. This is shown on the coupons in Figure 7.32. It seems to most viewers that the samples labeled Chemical 1 and Chemical 3 have less corrosion than those labeled Chemical 2 and

**Figure 7.33** Automated image analysis images of the same coupons shown in Figure 7.32.

Chemical 4. How much difference is noted depends on the technician doing the evaluation. Figure 7.33 shows images analyzed by a standard automated image processor. The instrument was set to identify locations where the images in Figure 7.32 had a certain predetermined density. The high-density locations (pits) are shown in Figure 7.33 as white images, somewhat like a negative of the images in Figure 7.32. Automated counting of the images revealed the information shown in Table 7.3, which clearly shows that Chemicals 2 and 4 are less effective in preventing corrosion than the other two chemicals and produce more corrosion than applying seawater to the same alloys.

The use of automated image analysis techniques eliminates differences of interpretation between different evaluators and also removes the tendency of human evaluators to respond differently at various times, for example, due to being tired, overworked, or distracted. While automated image analysis results depend on instrument settings, for example, the density of an image that will be read as a pit, once these settings are in place, the instrumentation will always interpret in the same manner. These techniques cannot be used in the field, but they are available in the laboratory.<sup>43-49</sup> A variety of techniques are now available that can survey

**TABLE 7.3 Pitting Results Determined by Automatic Image Analysis**

Chemical	ASTM Rating	Area mm <sup>2</sup>
Chemical 1	A-3	0.018
Chemical 2	A-4	0.385
Chemical 3	A-2	0.085
Chemical 4	A-5	0.785
Seawater	A-3	0.132

pitting profiles, determine pit density, and so on. Most metallurgical uses of automated image analysis have been for grain size, inclusion density, and phase analysis, but there is no reason why corrosion pit density cannot be routinely automated as well.

**Types of Standardized Test Procedures** NACE and other organizations have prescribed test procedures for a number of different purposes including testing for H<sub>2</sub>S resistance,<sup>50</sup> coatings suitability for various environments, elastomer and polymer performance, corrosion inhibitor effectiveness, etc. Some of these tests, for example, for coatings performance, require exposure times as long as 5000 h (approximately seven months). These long-term laboratory tests are often used after short-term screening tests reduce the number of candidate materials or procedures.

Laboratory tests are useful for screening candidate materials, but field exposure is the ultimate test. Field trials of various materials do not have NACE standards, but the laboratory testing procedures described in the various NACE test manuals provide guidance on how the results of field trials can be evaluated.

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## OILFIELD EQUIPMENT

Previous chapters have covered the fundamentals of metallurgy, corrosion control, inspection, and corrosion monitoring. This chapter discusses materials and corrosion control concepts associated with specific types of oilfield equipment. No single book can possibly cover all of the subjects necessary for a complete understanding of this very complex subject. This chapter is an attempt to indicate some of the more important concepts, from both economic and safety/reliability standpoints, associated with materials selection and corrosion control in oilfield operations.

Drilling operations, wells, pipelines, and flowlines present problems unique to oil and gas production and are discussed in detail. Other subjects, for example, facilities and process equipment and fasteners, are covered in less detail, because the materials and corrosion issues are not unique to oil and gas production and are discussed in great detail in other publications. As an example, floating production, storage and offloading (FPSO) vessels are very similar to moored ships, and much of the materials and corrosion control technology associated with them is derivative from that used for vessels that move cargo instead of being moored and stationary for long times. Similar comments would apply to newer forms of offshore production platforms, for example, spars and tension-leg platforms.

### DRILLING AND EXPLORATION

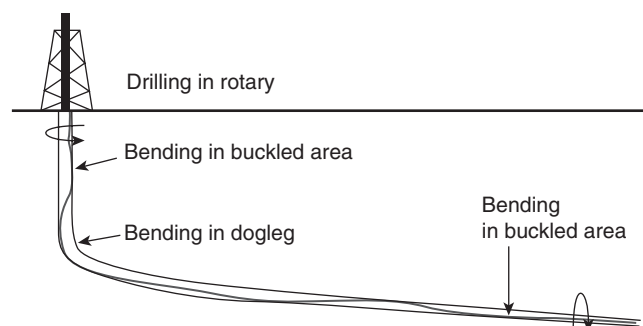
Drill strings are composed of high-strength materials, normally carbon steel with low-alloy connections. The

most common forms of material failure in drilling are fatigue and corrosion fatigue.<sup>1-4</sup> Other forms of corrosion, including environmental cracking, are also important.<sup>4-6</sup> Most problems in drilling are associated with the drill string, at least in part because downhole size restrictions necessitate the use of high-strength materials at stresses close to their operating limits. At one time, drill string failures due to torsion failures (“twist offs”) and tensile overload were common,<sup>6</sup> but the incidence of these failures has been reduced in recent years.<sup>4</sup> One in seven wells experience problems, and fatigue is the leading cause of drill string incidents, which can cost hundreds of thousands of dollars in downtime costs.<sup>2</sup>

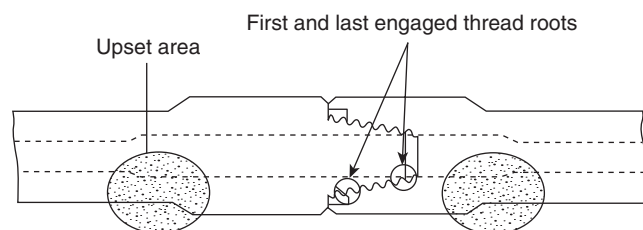
One of the practices leading to fatigue problems is the widespread use of directional drilling, which places high stresses at several locations within the drill string (Figure 8.1). Within a single joint, the locations most likely to produce fatigue cracking are near the ends where cross-section areas change (Figures 8.2 and 8.3).

At one time, there were major problems with cracks located near the last engaged threads on joints. Improved designs of both the pin and box ends of drill pipe have minimized these problems (Figure 8.4). Many proprietary connection designs are currently available.

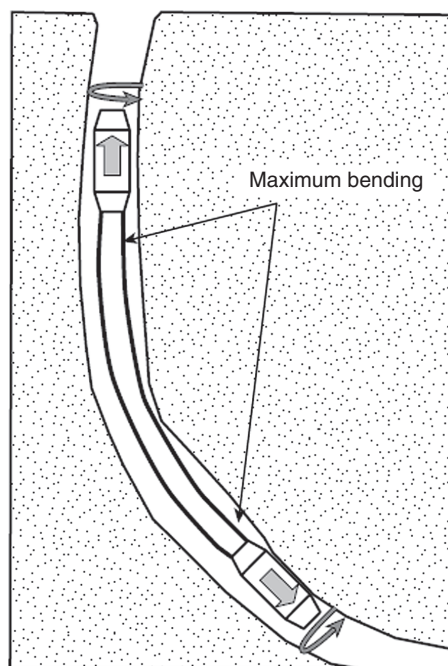
It is common for suppliers to list drill pipe by the American Petroleum Institute (API) standard designations along with descriptions of the type of connections available.<sup>7,8</sup> The necessity for drilling to greater depths plus horizontal drilling requirements, especially offshore, have led to the development of high-strength drill pipe and connectors that are not covered by API or other international standards. These are reported in the technical literature, and a variety of proprietary,



**Figure 8.1** Locations where drill string fatigue is likely.<sup>2</sup>



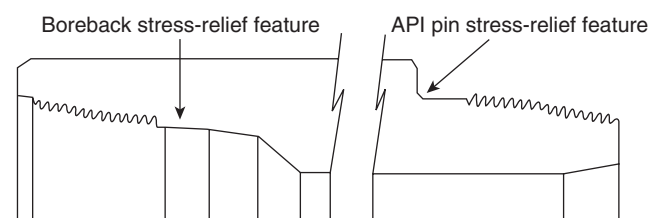
**Figure 8.2** Critical drill pipe fatigue areas.<sup>2</sup>



**Figure 8.3** Locations of maximum bending stresses on drill pipe in doglegs (bends) in drilling holes.<sup>2</sup>

experimental high-strength, and  $H_2S$ -resistant materials are commercially available.

Cumulative damage to drill pipe is important in determining remaining fatigue life.<sup>9</sup> Early efforts concentrated on records showing the number of trips (downhole insertions) of pipe, but recent efforts also



**Figure 8.4** Stress reduction by elimination of sharp features and cross-section changes.<sup>2</sup>

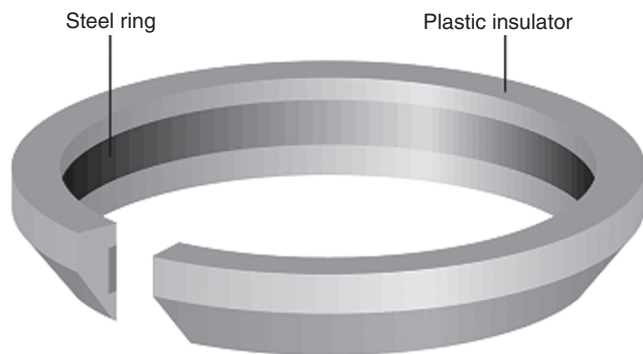
recognize differences based on where in the drill string the pipe has been located. The top of the string normally has the highest tensile loading, but other locations, as shown in Figure 8.1, can also experience very high loads.

Drill pipe strings are withdrawn from the hole for various reasons. It is recommended to break different joints on each trip out of the hole. Drill strings are normally broken in a manner that each pin and box connection can be inspected on every third trip. These visual inspections look for signs of wear, galling, and washouts (indications of fatigue cracks or pitting being enlarged from the inside out). Periodic inspection for fatigue cracks using magnetic particle inspection is enhanced by the use of fluorescent particles and ultraviolet (black light) illumination.<sup>1</sup> It is important that this inspection be concentrated near the locations shown in Figure 8.3.

The above discussion has concentrated on mechanical fatigue loading. It is important to recognize that most fatigue failures in drilling operations are actually corrosion fatigue problems, and any means of lessening the corrosivity of the environment will serve to prolong the life of drilling components.<sup>1,3,10</sup>

The primary means of controlling drilling fluids corrosion is by control of the drilling mud pH. Sodium hydroxide is usually used to maintain pH levels, and pHs are maintained at levels higher than necessary for optimal drilling mud performance. Typical pH ranges for mud-based drilling fluids are between 8.5 and 11, and higher pHs serve to reduce corrosion. Most reasons for keeping drilling mud pH under control are for fluid rheology purposes, but corrosion control is also maintained, and it is common to maintain the pH somewhat higher than necessary for rheology reasons in order to control corrosion. The ideal pH for many clay-based drilling fluids is 9, but corrosion control often results in pHs as high as 11. These high pHs are normally less corrosive, and they also tend to reduce the concentrations of  $CO_2$  and  $H_2S$  dissolved in drilling fluids.

Other means of controlling corrosion in drilling operations include the use of chemical oxygen and  $H_2S$  scavengers, and the use of internal coatings on drill pipe.<sup>1,3,4,11,12</sup> Air, and thus oxygen, is often introduced



**Figure 8.5** Drill pipe corrosion ring coupon fabricated in accordance with API RP 138-1B.<sup>3</sup> Image copyright Schlumberger Ltd. Used with permission.

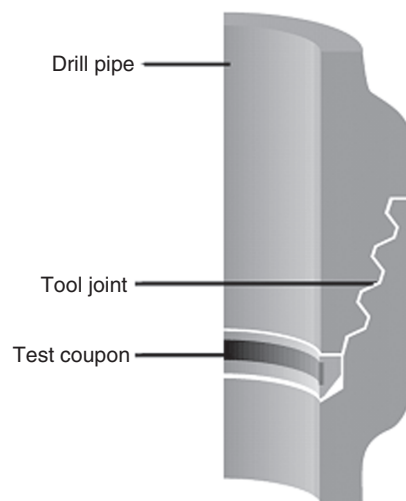
into drilling fluids during topside operations when downhole materials are separated from the fluids before they are recycled into the wellbore.

Lower-pH drilling fluids, for example, polymers and clear brines, require greater attention to oxygen scavengers and other corrosion-inhibiting chemicals than the use of clay-based muds. The use of filming corrosion inhibitors has been recommended in the past,<sup>11</sup> and these inhibitors, often necessary in polymer or clear drilling fluids, tend to attach to most solid surfaces, so their efficiency in mud-based drilling fluids is questionable. They are often applied to freshwater rinses that are often used to clean drill pipe after use prior to storage.

The effectiveness of drilling fluid additives in controlling corrosion (and thus corrosion fatigue) is monitored using ring-shaped corrosion coupons like those shown in Figure 8.5. These rings are inserted between the tool joint (Figure 8.6) at the top of the first stand above the drill collar and should usually be left in place for at least 40 h (usually 100 h). The ring is then sent to a laboratory for weighing and analysis.<sup>1,13–15</sup> Initial corrosion rates in the first few hours are usually faster and may give misleading results; this is the reason for waiting at least 40 h before pulling coupons. As in all corrosion monitoring, coupons can only indicate changes in corrosivity and cannot indicate true corrosion rates. They are used by drilling operators to determine the efficiency of chemical corrosion control measures, which can be adjusted as necessary.

Various inspection techniques have been reported for drill pipe, but their cost-effectiveness is questionable.<sup>2</sup> The best approach seems to be to track the usage history of the pipe in question and to retire it before fatigue problems become likely.

The high strength levels necessary for drill pipe and associated connections means that they cannot be manufactured in accordance with the guidelines for H<sub>2</sub>S



**Figure 8.6** Drill pipe corrosion coupon inserted in tool joint.<sup>3</sup> Image copyright Schlumberger Ltd. Used with permission.

service suggested in NACE MR0175/O 15156, which address long-term service in H<sub>2</sub>S environments.<sup>16</sup>

Aluminum drill pipe, sold primarily for its strength/weight advantages, does not have H<sub>2</sub>S cracking problems, and other attempts to develop H<sub>2</sub>S-resistant drill pipe and connections have been reported. The relatively short times of exposure to H<sub>2</sub>S environments minimize this problem, but drill strings are still subject to environmental cracking. Most control of this problem is due to pH adjustments which keep the pH of most drilling fluids in pH ranges (typically between 8.5 and 10) where H<sub>2</sub>S levels are minimized in bentonite clay drilling muds. Polymer and clear brine drilling fluids require the use of more aggressive H<sub>2</sub>S scavengers, usually zinc compounds. Zinc carbonates work well in high-pH environments, and the more expensive zinc chelates are used in brine-type drilling fluids. In both cases, they work by causing the precipitation of insoluble zinc sulfides. Iron-based magnetite (iron oxide approximately Fe<sub>3</sub>O<sub>4</sub>) is also used, but the efficiency is lower except at low pHs, which are not desirable for both corrosion control and rheological reasons.<sup>1</sup> The ability to withstand relatively long-term exposure to low levels of H<sub>2</sub>S does not impart immunity to H<sub>2</sub>S “kicks” where high levels of H<sub>2</sub>S may occur for periods of up to several hours.<sup>17,18</sup> While no NACE standard covers drilling equipment in H<sub>2</sub>S environments, a Canadian Industry Recommended Practice is available.<sup>19</sup>

Corrosion of drill pipe during storage is a concern. This is normally handled by washing the inside of drill pipe with fresh water after use. The use of corrosion inhibitors has also been reported,<sup>9,12</sup> and the widespread use of internally coated pipe also helps.



**TABLE 8.1 Corrosion-Resistant Alloys Available for Oilfield Wirelines**

UNS Designation	Common or Trade Name	PREN <sup>a</sup>	Critical Pitting Temperature (CPT)	
			°F	°C
S31600	316	26	72	22
S32305/S31803	2205	36	108	42
S20910	XM 19	38	106	41
N08028	28	40	129	54
N08926	25-6MO	47	149	65
S31277	27-7MO	56	176	80
R30035	MP35N	53	183	84

<sup>a</sup> PREN, pitting resistance equivalent number = Cr + 3.3 Mo + 30N.

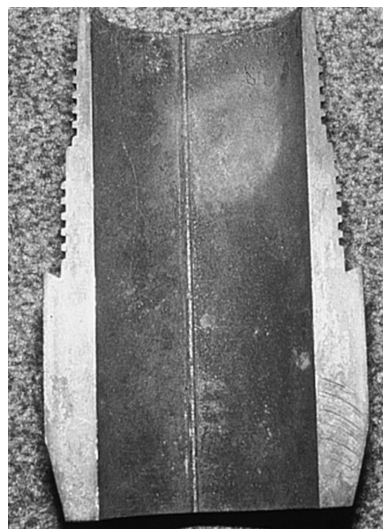
External wear of drill pipe is controlled by the use of hard bands, wear-resistant metal deposits on the outside of the box ends of tool joints. New drill pipe is available with factory-applied hard bands, and hard banding can also be applied to used drill pipe. Water cooling is necessary to prevent degradation of internal coatings during reapplication of hard facing to used drill pipe. Hard facing limits wear on the external diameter of the drill pipe, and it also reduces wear on casing.<sup>12</sup>

### Wireline

Oilfield wireline is supplied for a variety of downhole measurement and control purposes. It is made available from both carbon steel (often termed “plow steel” to imply high-carbon steel with high yield strengths usually obtained by extensive cold working) and corrosion-resistant alloys (CRA). Table 8.1 shows several CRAs available for wirelines. Many wireline suppliers use proprietary trade names for the alloys being supplied, but a quick Internet search can usually identify the Universal Numbering System (UNS) numbers associated with these alloys. Crevice corrosion of multistranded wireline is one possible problem with these lines, and high pitting resistance equivalent numbers (PRENs) are sometimes considered to be indications of alloys appropriate for this service.

Wirelines and their attached tools can cut internal coatings (Figure 8.7) and cause subsequent corrosion problems.<sup>20,21</sup>

High-strength wire is subject to hydrogen embrittlement in sour wells. Carbon steel wireline can be used in well fluids only because grease coatings on the metal surface prevent wetting of the wire and the absorption of hydrogen. Some hydrogen is inevitably absorbed into the metal, and allowing the hydrogen to bake out between trips is necessary. These bake-out times are



**Figure 8.7** Wireline damage to the internal coating on drill pipe.<sup>20</sup>

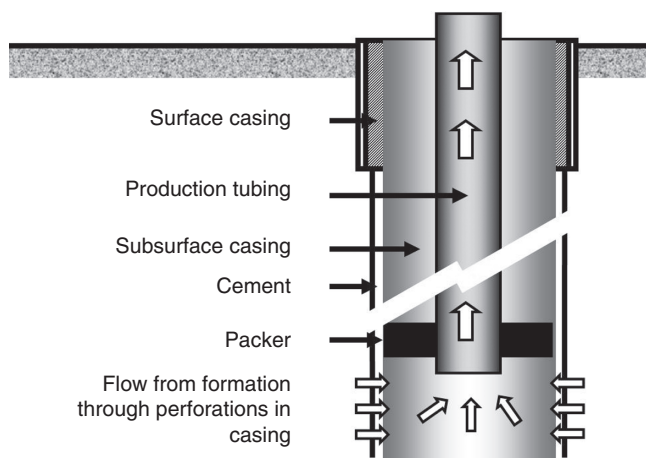
normally several days long and must be used for all wireline metals. The use of CRAs reduces, but does not eliminate, the tendency for hydrogen uptake.

### Coiled Tubing

Coiled tubing is used for many of the same purposes as wireline.<sup>22–24</sup>

The principal advantage of coiled tubing is the stiffness of the tubing which allows it to be “pushed” along horizontal legs in deviated wells. For workovers and other short-term applications, the exposure time is relatively short, hours or days, and corrosion can be a minimal concern. Fatigue becomes the major consideration in determining tubing life, because of the large strains induced during laying from reels. The number of trips for coiled tubing is limited to dozens of trips at the most. Unfortunately, the use of coiled tubing in H<sub>2</sub>S environments can produce problems even with short-term exposures, and clear guidance on appropriate approaches to avoid system failures is lacking.<sup>24,25</sup> Coiled tubing is also used for velocity tubing when the natural pressure in gas wells has degraded. The insertion of smaller-diameter tubing is used to increase fluid velocity restoring production and the removal of liquids from the wellbore. Velocity tubing may be used for years, and conventional corrosion control methods, usually with inhibitors, are employed.

CRA tubing is available and is used in some applications. These applications of coiled tubing are more likely to be used for subsurface controls and other long-term applications, for example, power to hydraulic lift pumps.

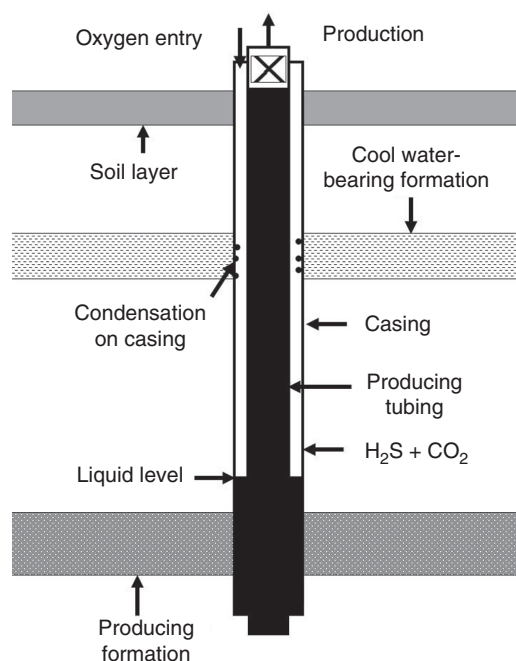


**Figure 8.8** Simplified schematic of an oil well.

## WELLS AND WELLHEAD EQUIPMENT

Wells are the oilfield equipment with the most corrosion problems. Reasons for the corrosivity of downhole environments include relatively high downhole formation temperatures, the effects of high pressure on solubility of corrosive gases (primarily  $\text{CO}_2$  and  $\text{H}_2\text{S}$ ), and the tendency of many newer wells to be developed at greater depths and temperatures. This is coupled with the difficulty of monitoring downhole corrosivity. Most corrosion monitoring is done near the wellhead, and unrecognized conditions downhole may not be recognized. To cite just one example, a frequently used means of monitoring wellbore corrosion is by iron analysis (iron counts) in the production fluids. This relatively insensitive technique is unlikely to detect pitting or other localized corrosion occurring at isolated locations on production tubing strings that may be thousands of meters (or feet) long.

Figure 8.8 is a simplified schematic of a typical oil well. The produced fluid, normally a combination of crude oil, natural gas, and water, is produced up the center production tubing. The well is separated from the downhole environment by metallic casing or liners. Casings are normally cemented to the adjacent formation and are considered permanent installations in the well. Liners serve a similar purpose, separating the production tubing from the wellbore, but they are not cemented in place and can be removed. It is common to have packers to separate the formation liquids from the annular spacing between the production tubing and the larger-diameter casing, but many wells, for example, gas wells and gas-lift wells, may be completed with no packers. Packers prevent produced liquids from rising too high in annular spaces. It is common to have downhole pumps to bring oil to the surface, and the produc-



**Figure 8.9** Locations where downhole components of an oil well are likely to corrode.

tion string is hung in the well from high-strength tubing hangers. Tubing hangers are suspended at the wellhead which also has valves, controls, and other devices. Pumps and wellhead equipment are discussed at the end of this section of wells.

Locations where downhole oil well components are likely to corrode are shown in Figure 8.9 and include:<sup>20</sup>

- The interior surfaces of production tubing strings, as well as tubing hangers, wellhead, and Christmas tree components, at locations where they are in contact with corrosive produced or injection fluids. Production tubing interiors are the most likely locations for downhole corrosion. Tubing and wellhead component corrosion can be minimized by proper material selection (usually CRAs), the use of internal coatings, or the use of corrosion inhibitors.
- Internal surfaces of the casing and the exterior of the production tubing exterior if the fluid in this space is filled with corrosive liquids or gases. If air leaks into the top of the annulus, corrosion can occur in the upper regions of the casing-production tubing annulus even in the presence of corrosion-inhibited packer fluids. While the strict definition of fluids includes liquids, vapors, and supercritical fluids, the term packer fluid is understood to mean a liquid or mud used to fill the casing-tubing

annulus to shut off the pressure of the formation fluids and to prevent them from rising in the annulus.

- External casing corrosion, especially where external formations produce changes in temperature, causing condensation in wells having no packer fluid liquids.

The produced fluid interface between the vapor-filled annular space and the bottom-hole liquid can become corrosive.

The drawings in Figures 8.8 and 8.9 are simplified, and many other components are found in most wells. It is also simplistic to show wells having vertical boreholes. Deviated wells like those shown in Figure 8.1 are becoming increasingly common, not only offshore, but also in environmentally sensitive areas. Downhole conditions in deviated wells are sometimes similar to deep pipelines, and many of the corrosion problems in pipelines will also be found in deviated wells. The principal differences between deviated wells and pipelines are the much higher temperatures and pressures common to well strings. Internal pipeline environments can be controlled to a greater extent than in wells, where the downhole temperatures and pressures cannot be changed.

### History of Production

Figure 8.10 shows the production profile for a typical oil field. Peak production normally takes several years to develop, and this is followed by gradual declines in volume. It is common to develop oil fields based on the idea that they will be in production for approximately 30 years.<sup>26</sup> As production goes down, money for maintenance decreases at times when the needs for maintenance and inspection increase. There are many fields that have been profitably producing oil for more than 50 years and, as the prices of hydrocarbon fuels increase, the extension of field life to even longer production cycles is likely.

As the prices of hydrocarbons change, many fields considered uneconomical become profitable again. It is not unusual to keep wells in production, especially oil wells, for example, offshore, because this is less expensive than removing them from service and dismantling the associated production equipment, offshore production platforms, and so on. When production fields age, downhole pressures degrade, especially for gas wells. The resultant changes in pressure-dependent produced fluid compositions alter corrosivity. Oil wells produce increasing formation water cuts, and this changes many oil fields from noncorrosive to corrosive at times when income levels, which often determine maintenance and inspection budgets, decline. Injection water break-

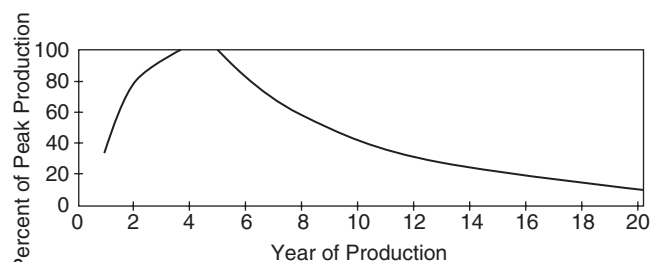
through also changes the corrosivity of produced fluids. All of these trends have led many operators to alter their design procedures to emphasize materials selection and maintenance programs that will require higher capital costs for more CRAs instead of relying, as in the past, on the use of corrosion inhibitors to minimize the corrosion of carbon steel downhole components.<sup>26,27</sup>

### Downhole Corrosive Environments

Oil is not corrosive to carbon steel in the absence of liquid water, so crude oils with low water cuts, where water is suspended as small droplets surrounded by oil (emulsified), are generally not corrosive. This was shown in Figure 3.1, which shows how corrosion rates of oil well production tubing change with water cut, and in Figure 3.2, which shows the idea of emulsified water surrounded by oil in deviated (nonvertical) oil wells.

Most oil wells also produce varying amounts of formation waters that are typically very high in dissolved minerals to include chlorides and other ionic salts. Formation waters can become corrosive, but only if oxygen or other reducible species are also present. In the producing formation the formation water is saturated with dissolved minerals. Changes in temperature and pressure as these fluids move up can lead to dissolved gas breakout, which may cause corrosion, and to the precipitation of mineral scales which may not only be protective but may also lead to localized corrosion at breaks in the scale and to scale plugging of tubing (Figure 3.24). The natural buffering action of dissolved minerals in formation waters often prevents or minimizes corrosion, and dissolved chemicals often buffer the water, preventing the formation of acidic water by dissolved gases such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$  which may also be in the fluid stream. In summary, many oil wells are noncorrosive or are minimally corrosive.

The presence of high levels of  $\text{CO}_2$  in oil wells can cause corrosion (sometimes called “sweet corrosion”) under conditions where mineral deposit scales are not protective.<sup>20</sup> Increasing corrosion rates after a critical water cut appears (approximately 40–50% depending



**Figure 8.10** Production profile for a typical oil field.

on the field) can be detected by monitoring corrosion rates on the surface or by downhole caliper surveys. For many oil wells, this is when downhole corrosion inhibitor injection is started. Unfortunately, when corrosion is detected, for example, by caliper surveys indicating approximately 10% wall loss, the tubing surface has been roughened and covered with corrosion products. This makes the introduction of successful corrosion inhibitor programs difficult, especially without prior downhole cleaning. Some operators are reluctant to wait for corrosion to happen before starting corrosion inhibitor programs.<sup>26</sup>

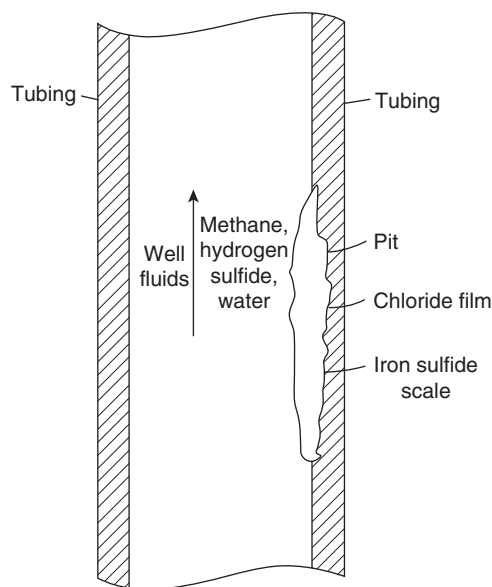
Natural gas is not corrosive provided it remains in the vapor state, but most gas fields are considered corrosive from the beginning of production. Wells may not be corrosive if the production streams reach the surface under appropriate temperature and pressure conditions. Once lowered temperature and pressure conditions allow condensation of higher-end organic molecules and water, gas condensates usually become very corrosive. Corrosion often appears at intermediate levels in production tubing (Figure 8.11) as localized corrosion at imperfections in iron carbonate or other protective films.<sup>3,28-31</sup> These imperfections can occur anywhere on the tubing, but they are more likely to happen at joints or other areas of flow disturbance and can be minimized by using premium low-turbulence joint connections.

The reason for corrosion in CO<sub>2</sub>-rich condensate environments is the condensed liquids are low in mineral content, so they do not form the thicker protective

scales likely to be formed in oil wells, where mineral-saturated formation waters are being coproduced. Pure water is more ionic at elevated temperatures (Figure 2.8), and this makes elevated temperature condensates in producing wells corrosive. Condensates have little buffering capacity. They will be acidic and corrosive to a far higher degree than the high-mineral content formation waters that wet the interiors of oil well tubing. Condensates of CO<sub>2</sub> and water are highly corrosive, and the presence of any organic acids (acetates, formic acids, etc.) greatly increases their corrosivity.<sup>26</sup> Temperature zones and their resulting rate-determining factors in CO<sub>2</sub> environments at various temperatures were illustrated in Figure 3.19. Note how the protectiveness of iron carbonate scales changes at approximately 60°C (140°F) and increases with increasing temperature at deeper locations. This means that many gas wells do not need corrosion inhibitors in their lower, high-temperature locations.

Gas well pressures change with time. Initial formation pressures can be fairly high, but as production progresses, the pressures, but not the temperatures, of formations change and become lower. Table 8.2 shows the changes in water solubility in natural gas at two different temperatures only 20°F (11°C) apart. As production proceeds and formation pressures decrease, the relative amount of water in produced natural gas increases. This means that, like oil wells, the corrosivity of gas wells is likely to increase.<sup>26</sup>

Chemical influences on CO<sub>2</sub> corrosion were discussed in detail in Chapter 3, Corrosive Environments. Figures 3.14–3.18 illustrate various aspects of CO<sub>2</sub> corrosivity. There are no universally accepted standards or models for CO<sub>2</sub> corrosivity. This is a subject of continuing research, and consensus is unlikely in the foreseeable future. Various CO<sub>2</sub> corrosivity prediction models are available.<sup>1,26-33</sup> Figures 3.17 and 3.18 are associated with



**Figure 8.11** Barnacle corrosion in production tubing.<sup>3,28,29</sup> Reprinted with permission of ASM International. All rights reserved. <http://www.asminternational.org>.

**TABLE 8.2** Solubility of Water in Gas under Reservoir Conditions<sup>26</sup>

Reservoir	Water Solubility	
Pressure	In Gas, bbl/MMscf	In Gas, bbl/MMscf
Bara (psia)	127°C (260°F)	138°C (280°F)
239 (3460)	2.4	3.2
207 (3000)	2.6	3.6
172 (2500)	3	4
138 (2000)	3.5	4.7
103 (1500)	4.3	5.9
68 (1000)	6	8.3
34.5 (500)	11.2	
27.6 (400)	13.8	



CO<sub>2</sub> corrosion models developed by K. DeWaard and coworkers, which are some of the first mathematical models to have been proposed. These early models have been widely adopted and discussed. Many operators find that the corrosion rates predicted by the DeWaard and associates approaches tend to predict corrosion rates higher than experienced in field exposures. Most of the newer models do an excellent job of predicting corrosion rates under the controlled laboratory testing conditions used for their development, and they have been verified by laboratory experimental data. Unfortunately, unidentified or non-included field conditions, often minor production fluid constituents, are not recognized in these models, and predicted corrosivity in the design process must be confirmed by monitoring and testing once production starts.<sup>26</sup> Changes in produced fluid characteristics also necessitate continuous monitoring, especially for gas wells.<sup>26,27,33</sup> As produced fluid corrosivity increases, the need for more diligent monitoring and inspection also increases. This often happens at times when decreased production rates suggest to management that lowered inspection and maintenance budgets, which are often based on field production income, tend to also decrease.

CO<sub>2</sub> or sweet corrosion is the most common environmental problem causing weight loss corrosion in oil and gas production. H<sub>2</sub>S is substantially less corrosive, as was shown in Figure 3.3, which compares the influence of dissolved oxygen, CO<sub>2</sub>, and H<sub>2</sub>S on water corrosivity. Unfortunately, H<sub>2</sub>S, or “sour” weight loss corrosion as it is often termed,<sup>20</sup> is not the only problem associated with H<sub>2</sub>S production. Absorbed hydrogen from H<sub>2</sub>S can also lead to various forms of hydrogen-related cracking.

While the term “sweet corrosion” has historically been used to indicate oilfield corrosion under conditions where dissolved CO<sub>2</sub> in the aqueous phase lowers *in situ* pHs, it is also used to differentiate between conditions where the downhole fluids have enough H<sub>2</sub>S to come under the guidance of NACE MR0175/ISO 15156. The parallel term “sour corrosion” implies corrosion in fluids with enough H<sub>2</sub>S for MR0175/ISO 15156 to apply.

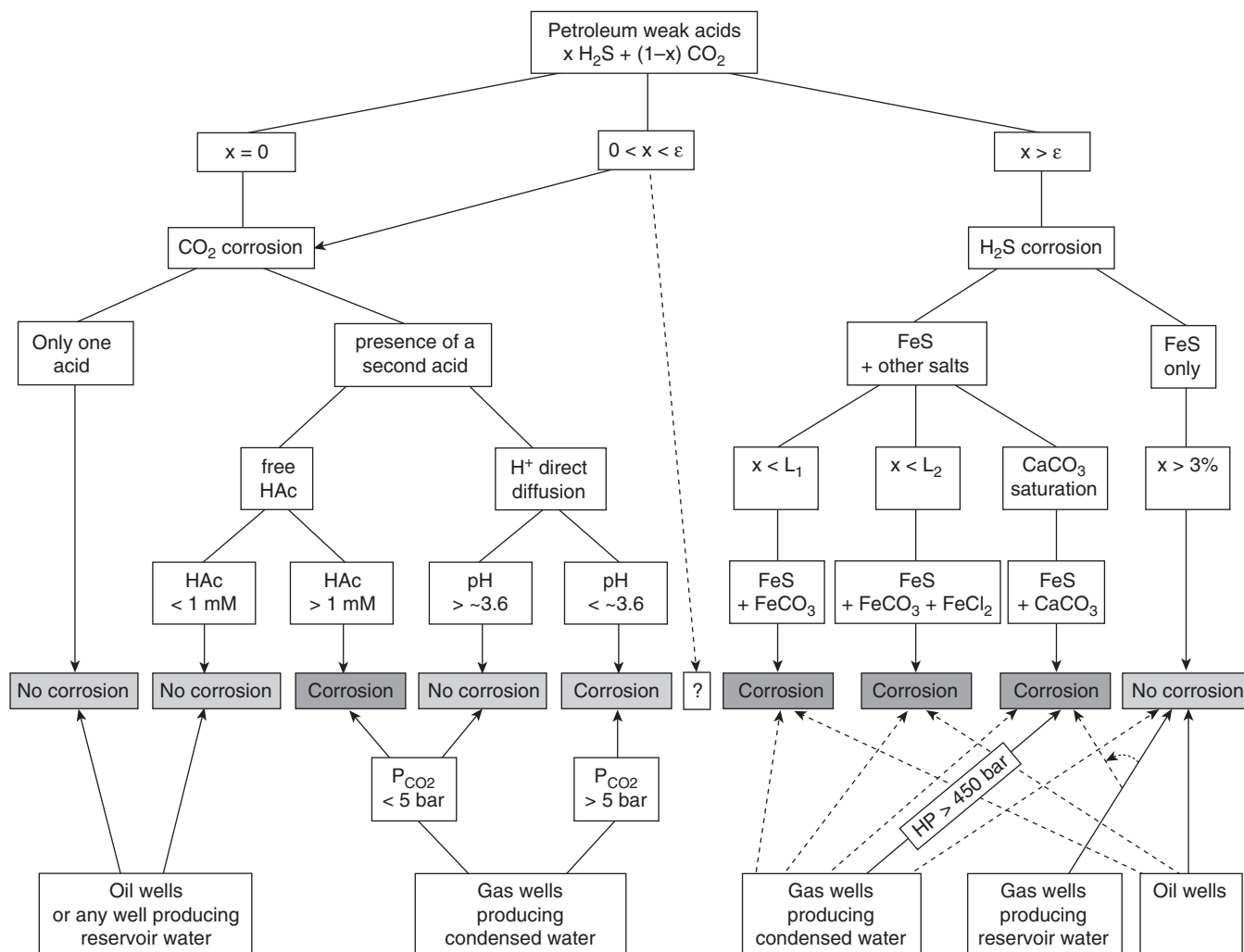
Most new oil and gas wells are now completed under the assumption that they will eventually become “sour” and produce undesirable levels of H<sub>2</sub>S. The appropriate guidance for these designs should usually be NACE MR0175/ISO 15156 with the publication date specified.<sup>16,26,28,34,35</sup> This standard, like many others, undergoes periodic updates and changes, and it is important that the appropriate version of any standard be understood by all parties concerned, often several decades after the design and installation of original equipment has been accomplished.<sup>36</sup> Readers are cautioned that MR0175/

ISO 15156 is primarily concerned with hydrogen-related cracking phenomena.

Weight loss corrosion can also occur under high-temperature high-pressure downhole conditions. The models for H<sub>2</sub>S corrosion are less widely known and are not often used. The scales formed by downhole H<sub>2</sub>S corrosion are often hard and compact, unlike the more porous carbonate scales formed in CO<sub>2</sub>-rich environments. Relatively thick iron sulfide corrosion products can restrict flow in a manner similar to the scales formed from carbonate or other mineral-rich fluids. Unlike the scales shown in Figure 3.24, which come from precipitation of produced fluids as temperature and pressure conditions change in wells, this plugging is due to corrosion, but it can have the same undesired effect of restricting oil well production rates.<sup>31</sup>

A recent report discusses weight loss corrosion and proposes explanations for corrosion in H<sub>2</sub>S-containing waters. The parameters associated with when weight loss corrosion occurs in wells containing H<sub>2</sub>S and/or CO<sub>2</sub> are illustrated in Figure 8.12.<sup>31</sup> This model for corrosion prediction is very complicated, is only recently presented, and has not been confirmed by other operators. It only serves to illustrate how complicated an understanding of downhole corrosivity is likely to be. Predictive models are no substitute for monitoring and inspection once production begins, and changes in corrosivity as fields age are to be expected.

Most of the long-recognized environmental variables on corrosivity of oil and gas production are associated with three gases—oxygen, CO<sub>2</sub>, and H<sub>2</sub>S—and were discussed in detail in Chapter 3, Corrosive Environments. Less attention has been paid to the influence of organic acids. These relatively small organic molecules have similar molecular weights, and volatility, to the heavier components in natural gas. Examples of organic acid terms appearing in the oilfield corrosion literature include carboxylic acids (formic acid, acetic acid, propionic acid, etc.), formates, acetates, propionates, fatty acids, and oxalic acid. All of these organic acid formers have similar properties. As organic chemicals, they tend to be less ionic than mineral acids (hydrochloric acid—HCl, nitric acid—HNO<sub>3</sub>), but they can be significantly ionic and corrosive in some fluids, such as condensates, especially at elevated temperatures when they will tend to become more ionic than at lower temperatures. CO<sub>2</sub> pitting corrosion in the absence of organic acids may not occur. “There is no record of CO<sub>2</sub> corrosion in a producing well in the absence of acetic acid.”<sup>37</sup> This may only mean that whenever acetic acid (the second smallest of these organic acids) was present in natural gas streams, it was detected and reported while formic acid, which is smaller, plus propionic acid and other organic acids likely to have been in the same produced fluids, were

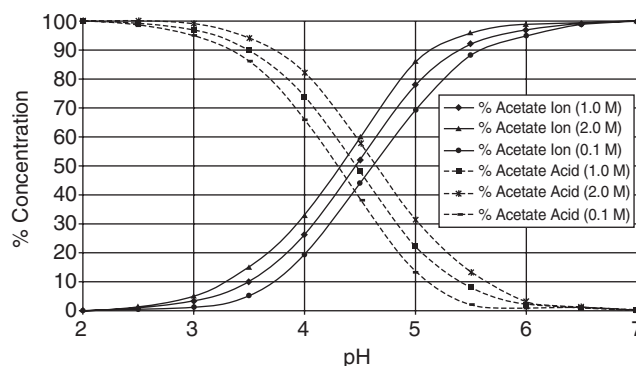


**Figure 8.12** Logigram for predicting corrosion in oil and gas wells in the presence of CO<sub>2</sub> and/or H<sub>2</sub>S as weak acids.<sup>31</sup> Reproduced with permission of NACE International.

not detected or reported. Virtually all Gulf of Mexico gas condensate wells produce detectable amounts of organic acids in the condensate, and organic acids are also reported to be a problem worldwide.<sup>36-40</sup>

Figure 8.13 shows the effect of pH on dissociation/ionization of acetic acid at room temperature. The ionization of organic acids would be even more pronounced at the elevated temperatures found in condensate-producing gas-well production streams. While these acids are not strong and are corrosive in many low-temperature applications, downhole conditions in gas wells with minimal buffering minerals in the condensate water can lead to very aggressive corrosive environments.<sup>41,42</sup>

Formation water is usually high in mineral content. Once it starts to be produced in gas wells, the mineral



**Figure 8.13** Dissociation of acetic acid at 25°C (77°F).<sup>41</sup>

content of the water in gas wells may increase and the pH changes and increases. The produced gas stream may become less corrosive when this happens.<sup>20</sup>

Injection fluids—water, steam, natural gas, CO<sub>2</sub>, or H<sub>2</sub>S—may eventually become part of production well fluid streams. Injection waters, even if they are reinjected formation waters, will have different chemistries and scaling tendencies than the original formation waters. The timing of injection water breakthrough will often be different for various wells in the same field. Changes in corrosion rates detected by electrical resistance probes or corrosion coupons are usually among the first indications that injection water breakthrough has occurred, although pH or electrical resistance probes would probably be more sensitive if they were in use.

Inadequate biocide treatment of surface waters will often result in souring of formation waters due to inadequate injection water treatment, and corrosion rates frequently increase when injection water breakthrough occurs.

Workover and formation treatment fluids may also affect corrosion of producing wells. This is usually controlled by monitoring corrosion rates after these operations and by adding increased corrosion inhibitors until the topside produced stream returns to the original, prior to treatment, corrosion rates. Coupons cannot detect these changes in corrosion rates, and electrical resistance probes are usually used.<sup>33</sup>

This section has reviewed downhole corrosivity in various types of wells. New oil wells are often not corrosive, and it is common to monitor corrosion rates and to not start corrosion inhibitor injection until a predetermined amount of corrosion, usually associated with increased water cuts, has occurred. A common starting point is once caliper surveys or other downhole inspections indicate a wall loss of 10%.<sup>26</sup> The major drawback to this approach is that by this time, the tubing surface may be roughened, and the effects of inhibitor treatments may be lessened and perhaps ineffective. Gas wells are usually considered corrosive from the beginning. While oxygen (usually due to leaks from the surface), CO<sub>2</sub>, and H<sub>2</sub>S are the primary contributors to corrosivity of produced fluids, the effects of organic acids are receiving increased attention in recent years. Simulation fluids and injection water breakthrough can also affect corrosivity. Many models are available to predict corrosivity in sweet or CO<sub>2</sub>-controlled corrosion, and MR0175/ISO 15156 is used to prevent cracking-related problems in H<sub>2</sub>S or sour environments. Unfortunately, these models are usually based on laboratory data and do not adequately account for many of the unrecognized variables in downhole produced fluids.

In the absence of produced fluid corrosivity data, the following guidance has been suggested for new wells:<sup>26</sup>

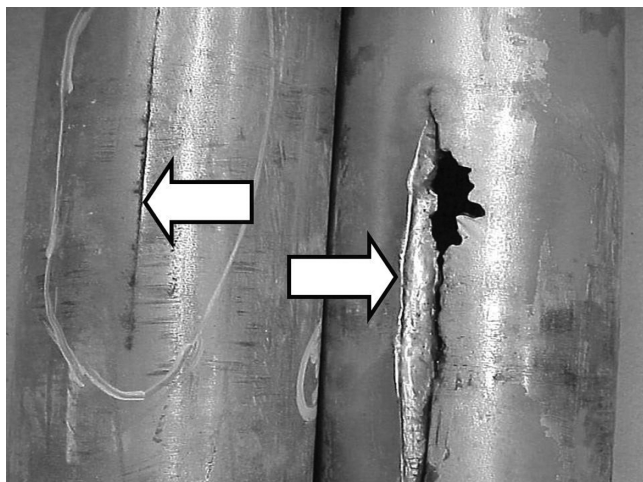
**Gas Wells** Assume condensed water pH based on fluid analysis and calculation of *in situ* pH.

**Oil Wells** Condensed water is too conservative, the produced fluids are unlikely to be that aggressive. Assume 200 mg/L alkalinity until produced fluid data is available.

The guidelines in the previous paragraph indicate the type of corrosion control that was common until quite recently. Most wells were completed with carbon steel tubing and casing.<sup>28</sup> Increased costs of component replacement, and the trend for wells to remain in production for even longer than the 30-year life that was once assumed to be the practical life limit of downhole tubing and equipment, have led many operators to install CRAs from the beginning, even in nominally nonaggressive conditions. The thinking behind this approach is that even one tubing string replacement at approximately 30 years is too expensive, and the incremental costs of installing CRAs (usually 13Cr tubing) on initial completion is good insurance against the costs of more than one million dollars per well associated with retubing a well.<sup>26,33</sup>

**Annular Spaces** The annular spaces between tubing and casing or liners are usually not used for production flow, but they are sometimes used for downhole treatments, for example, inhibitor injection. Most annular spaces are filled with packer fluids, primarily water-based liquids, but sometimes oil or muds. These fluids serve to shut off production from downhole pressure and to minimize the pressure differences between the outside of the tubing and the casing interior. These fluids are usually much heavier than water. Solids-free packer fluids can have specific gravities from 0.83 to 2.3. This density is usually achieved by the addition of soluble salts. These salt solutions, which must be very concentrated in order to increase the density of the brines, should not be very corrosive, and usually they are not. The reasons for this were illustrated using the ideas shown in Figure 3.6, which showed how the corrosion rate declines due to decreasing oxygen solubility in saltwater. Brines used for this purpose include sodium chloride, calcium chloride, calcium bromide, zinc bromide, and cesium formate.<sup>1</sup>

Corrosion inhibitor packages are usually included in packer fluids to minimize any possibilities of corrosion. Organic film-forming inhibitors are useful up to approximately 250°F (120°C). Beyond these temperatures, thiocyanate inhibitors have been used. Unfortunately, the thiocyanate ion (SCN<sup>-</sup>) can break down and form



**Figure 8.14** Cracks in duplex stainless steel downhole tubing caused by  $H_2S$  generated from degradation of the packer fluid. The wider crack on the right is caused by erosion of high-pressure fluids escaping into the tubing/casing annulus. This is a typical washout pattern.

$H_2S$  gases. Figure 8.14 shows duplex stainless steel tubing that cracked due to  $H_2S$  generated from packer fluid degradation downhole. The literature discusses several instances of problems of this type, and alternatives to thiocyanate corrosion inhibitors are under development.<sup>42–46</sup> No completely acceptable alternatives have been demonstrated to have long-term downhole stability.

**Types of Wells** The previous section contained a detailed discussion of the environmental variables that affect corrosivity in well environments. Most wells will experience a variety of these environments. The discussions that follow are intended to highlight the environments associated with the primary fluids being handled in various types of wells. The main differences between corrosion in oil, gas, and injection wells occur on the production tubing interior surfaces. Annular space corrosion is approximately the same for all of these types of wells and is usually controlled by packer fluid corrosion inhibitors as discussed above.

Most wells and associated wellhead equipment are completed with materials that meet NACE MR0175/ISO 15156 requirements. This is because operators have learned that even if the original formation and produced fluids do not contain  $H_2S$ , it is possible that they will “sour” and produce  $H_2S$  at some time in their production history. It is not unusual for wells to remain in production for much longer than the 30 years they have been typically assumed to be productive, and using  $H_2S$ -tolerant materials is much less expensive than retubing

at some later date. Well casings, which are considered permanent installations, are seldom removed or replaced.

**Oil Wells** Oil wells typically produce a combination of crude oil, natural gas, and formation water. Oil wells can be profitable when less than 10% of the produced liquid is oil and the rest is mineral-rich salty water. Corrosion control is not necessary in many wells until the water cut increases to the extent that tubing interiors become water wetted. Many operators wait until a predetermined corrosion rate or wall loss, typically 10% as determined by caliper surveys, before they begin corrosion inhibitor treatments.<sup>20</sup> The disadvantage of this approach is that once corrosion has started, corrosion inhibitors will be less effective due to their limited ability to penetrate beneath corrosion products and scale. Most oil wells start out with natural flow to the surface, but after time downhole pressures subside and artificial lift devices become necessary.

Many operators have adopted the policy of starting all new completions with CRAs, typically 13Cr tubing. Downhole equipment, filters, pumps, and so on, and wellhead equipment are typically made from CRAs. Galvanic corrosion is seldom a problem unless the downhole water becomes acidic due to injection water souring or the bottomhole formation water has a pH less than approximately 3.6 as shown in Figure 8.12.

**Gas Wells** Unlike oil wells, gas wells are usually corrosive from the start of their production. The reason for this is that most natural gas will contain varying amounts of water vapor as well as natural gas condensates, higher-molecular weight organic chemicals that tend to condense from the natural gas, which is typically more than 90% methane with a molecular weight of 16 compared to water at 18, formic acid at 46, acetic acid at 60, and so on. Liquid condensation is more likely as molecular weight increases, so it is inevitable that whenever water condenses on tubing interiors, it will be accompanied by higher-molecular weight organic acids. This means that whenever water condenses in a production string, it is likely to be in the presence of organic acids which lower the pH of the water and make it acidic and corrosive. Natural gas may also contain other corrosive chemicals, including elemental sulfur and mercury. While concentrations of these corrosive chemicals may be low and difficult to detect using normal analytical chemistry techniques, high-volume gas wells can eventually produce significant amounts of corrosive condensates. If these liquids are not suspended in the gas stream and removed from the well, they eventually cause downhole corrosion. At temperatures where organic filming inhibitors can work, the use of these inhibitors is the



preferred method of corrosion control. For deep, hot gas wells operating at temperatures where organic inhibitors break down, the use of CRAs is necessary.

While a number of software systems have been developed for the purpose of modeling gas well corrosion, they differ in their predicted corrosion rate outputs, and they are not at the stage of development where they can reliably predict corrosion rates prior to the start of production.<sup>26,27,32,33,47</sup> SOCRATES, a proprietary software package, is gaining wide use for selecting alloys for downhole applications,<sup>48</sup> and other software is under development. Nyborg reviewed the software available in 2009 and reported difficulties with all of the corrosion rate prediction models.<sup>32</sup> Most of the currently available models are not intended for use in the presence of H<sub>2</sub>S or organic acids.

**Injection Wells** Injection fluids are usually water or steam but sometimes gas, for example, natural gas, CO<sub>2</sub> or H<sub>2</sub>S, injected into reservoirs to either avoid pollution (disposal wells) or to maintain pressure. Enhanced oil recovery is also important using water flooding, steam injection and, in recent decades, miscible flooding with CO<sub>2</sub> which may be pipelined long distances to maintain production after less expensive means have neared or reached their limits.

Because injection water chemistry can be controlled, it is common to use carbon steel or 1% Cr for many injection wells, although fiber-reinforced plastic (FRP), and lined pipe are also used. If bottomhole conditions lead to corrosive water accumulation, the tubing and equipment at the bottom of the hole may have CRAs, usually 13Cr.

NACE RP0475 recommends metallic materials for injection water handling. It recommends carbon steels for use in non-aerated injection waters (less than 10ppb oxygen) with CO<sub>2</sub> partial pressures below 20kPa (3psi) and without H<sub>2</sub>S. Tables of alloys for other service are provided, including recommendations for various components on injection pumps, valves, filters, oxygen, and H<sub>2</sub>S strippers, and miscellaneous equipment to include storage tanks, gathering and injection lines, and downhole tubing.<sup>49</sup>

Most corrosion control of injection water is by gas stripping to remove dissolved oxygen. This method is used for seawater and surface waters intended for injection wells, because it is normally more cost-effective than vacuum deaeration. It can achieve part per billion levels of residual oxygen, but the lower limit depends on the quality of the stripping gas. Natural gas, exhaust gas from engines, or nitrogen are the normal stripping gases used for this purpose.<sup>20,50,51</sup> Oxygen scavengers are then added to the water bringing dissolved oxygen levels down to approximately 5–10ppb. Sodium bisulfite

(NaHSO<sub>3</sub>), ammonium bisulfite, (NH<sub>4</sub>)<sub>2</sub>HSO<sub>3</sub>, and sulfur dioxide (SO<sub>2</sub>) are some of the oxygen scavengers that are used for this purpose. Filming corrosion inhibitors are seldom used, because the large volumes of water involved mean that oxygen stripping and scavenging is more economical.

This discussion has concentrated on the use of surface waters for injection purposes. The handling of formation water prior to reinjection emphasizes maintaining positive pressures on all piping and vessels to minimize air entry. Oxygen scavengers are then added prior to reinjection.

Because injection water oxygen control is the primary means of corrosion control, it is necessary to monitor the oxygen levels at various stages in treatment and transport. This is done with online electronic oxygen sensors as well as galvanic probes and other means of corrosion monitoring. Galvanic corrosion probes that will respond quickly to changes in oxygen content are often the first indication that oxygen control has been compromised.<sup>52</sup>

Reservoir souring due to inadequate injection water treatment is a serious concern. This often happens several years after water injection has started and is usually due to inadequate water treatment to include the use of biocides that are effective on anaerobic bacteria. Seawater treatment must include some means of removing the natural sulfates present in seawater.<sup>53</sup>

### Tubing, Casing, and Capillary Tubing

Most corrosion problems in oil and gas production are associated with tubing and casing. The reason for this is the large volume of these components used per well. While it is common to use CRAs for wellhead equipment, pumps, packers, and so on, economic incentives and availability drive the trends for continued use of carbon steel and low-alloy tubing and casing. Concerns with eventual souring of fields have convinced most operators that all downhole equipment, to include tubing and casing, should meet the recommendations of NACE MR0175/ISO 15156.<sup>16,34,35,54</sup>

**Tubing Corrosion** Most well designs use tubing strings for upward production of produced fluids. Formation temperatures do not change during the lifetime of production, but production rates decrease as fields age. The resulting changes in temperature and pressure as fluids move up production tubing strings alter locations of gas breakout in oil wells and condensation formation in gas wells, and these altered locations are where most corrosion problems are likely to occur. Injection water breakthrough can also alter the corrosivity of both oil and gas wells. The cost of tubing replacement can be upward of

\$1 million per well, and many operators have adopted the policy of starting oil well production with 13Cr tubing in the hopes that they can avoid tubing replacement at some time in the future.<sup>26,32,33</sup> Gas well tubing may possibly require even more CRAs (duplex stainless steels or higher grades of CRAs). The models for predicting when these alloys are necessary are still under development and are controversial, but many operators do use software-based tools for tubing selection.<sup>28,32,33,48</sup> Table 8.3 shows the NORSOK standard recommendations for various well components to include tubing and liners.<sup>55</sup> Note that while recommendations for tubing and liners are identical for these removable and replaceable components, the table does not address casing, which is permanent and cannot be removed and replaced.

Additional methods of controlling production tubing corrosion include the use of corrosion inhibitors and interior coatings and linings. These methods of corrosion control are discussed separately after the discussions of tubing, casing, and capillary tubing.

**Casing Corrosion** Casing is the structural retainer for the walls in oil and gas wells. Approximately 75% by

weight of oil country tubular good (OCTG) shipments are for casing, which is intended to last for the life of the wells and not be pulled, inspected, or replaced. Corrosion of casing can be from either the interior, in the annular spaces shared with tubing exteriors, or on the exterior.

Internal casing corrosion in the annular spaces is discussed above and applies to both the casing interior and tubing exterior. Most corrosion control of casing interiors is by appropriate alloy selection and by packer fluid inhibitor use, either filming inhibitors at lower temperatures or oxygen, CO<sub>2</sub>, and H<sub>2</sub>S scavengers at elevated temperatures.

The annular spaces in new wells should be considered corrosive until caliper or other borehole inspections indicate that corrosion is at low or negligible levels. Pumping wells should be tubed as close to the bottom of the wellbore as possible to minimize corrosion damage to the casing, which is often concentrated at the liquid/vapor interface (Figure 8.9). Casing pumps are generally not advisable.<sup>1</sup>

Exterior corrosion protection is usually provided by cementing, which provides a high-pH noncorrosive

**TABLE 8.3 Materials Selection for Wells<sup>55</sup>**

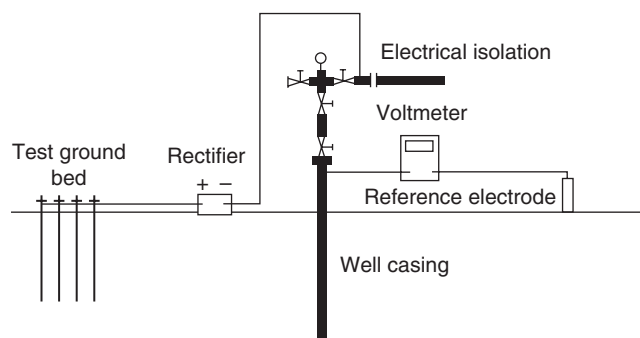
Well Type	Tubing and Liner	Completion Equipment (Where Different from Tubing and Liner)
Production	13Cr is base case Low-alloy steel for systems with low corrosivity 13Cr and 15Cr alloys modified with Mo/Ni, duplex and austenitic stainless steels and nickel alloys are options for high corrosivity	13Cr
Aquifer water production	13Cr is base case	
Deaerated seawater injection	Low-alloy steel	UNS N09925, Alloy 718, 22Cr, or 25Cr duplex stainless
Raw seawater injection	Low-alloy steel with glass-reinforced plastic (GRP) or other lining Low-alloy steel for short design life	Titanium or inhibitors in oxygen-free systems Titanium or inhibitors in oxygen-free systems
Produced water and aquifer water injection	Titanium or inhibitors for oxygen-free systems Low-alloy steel  Low-alloy steel with GRP or other lining	13Cr with same limitations as for tubing in this service 13Cr with same limitations as for tubing in this service
Gas injection	13 Cr. Provided oxygen < 10mg/m <sup>3</sup> 22Cr duplex, Alloy 718, N09925. Provided oxygen < 20mg/m <sup>3</sup>	
Alternating injection and combination wells	Materials selection same as for production wells Materials selection shall take into account the corrosion resistance of different materials options for the various media	

Data condensed from table 2, NORSOK Standard M-001, August 2004.

environment for the casing exterior, and by electrical separation at the wellhead with insulated flange assemblies that are intended to isolate the well from flowlines that could produce stray current corrosion. At one time, it was common practice to only cement the casing from the producing formation to seal the well annulus. Modern practice tends to cement the entire wellbore.<sup>54</sup> The reader is cautioned that many electrical isolation assemblies are shorted by maintenance and other work during the decades that wellheads are in service, and downhole corrosion due to stray electrical currents sometimes occurs. The only way to insure that this has not happened is to conduct periodic downhole inspections. It is not always economically feasible to electrically isolate wells from flowlines and other nearby equipment.<sup>56,57</sup>

External coatings are available that can withstand the mechanical damage associated with casing installation. These coatings, which will be damaged during installation, can reduce the cathodic protection current to approximately 10% of the current needed for casings with no external coating.<sup>54</sup>

Cathodic protection is not normally installed on well exteriors until condition surveys or leak records indicate that corrosion is occurring due to external casing corrosion. The electric current requirements for cathodic protection on casings is then determined on existing well casing by applying electricity to the casing exterior and plotting the current-surface potential data on a voltage versus log current ( $E \log i$ ) scale<sup>54,56-58</sup> (Figures 8.15 and 8.16). For the data shown in Figure 8.16, approximately 18 amps of current is considered necessary to protect the casing exterior. It is common practice to determine the current necessary for either each well in the field, for small fields, or for selected representative wells in larger fields. The currents necessary for each individual well are then supplied from a central rectifier and ground bed. Individual controls on the



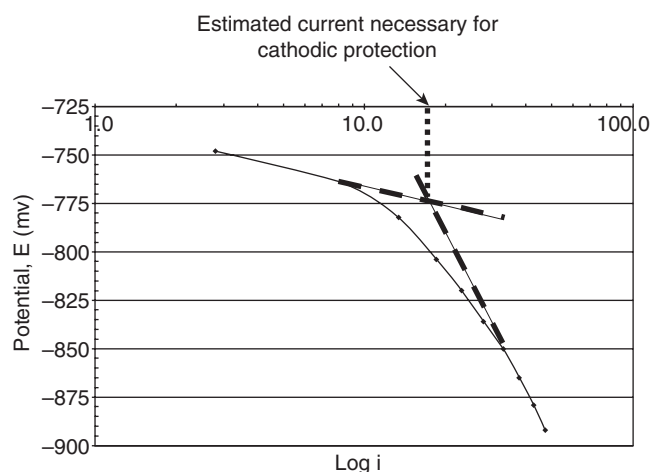
**Figure 8.15** Experimental setup to determine required cathodic protection current for existing well casing exterior.<sup>58</sup> Figure reproduced with permission from NACE International.

current leads to each well are necessary to prevent too much current from being drained into the low-resistance well denying adequate protection to other wells.<sup>32</sup>

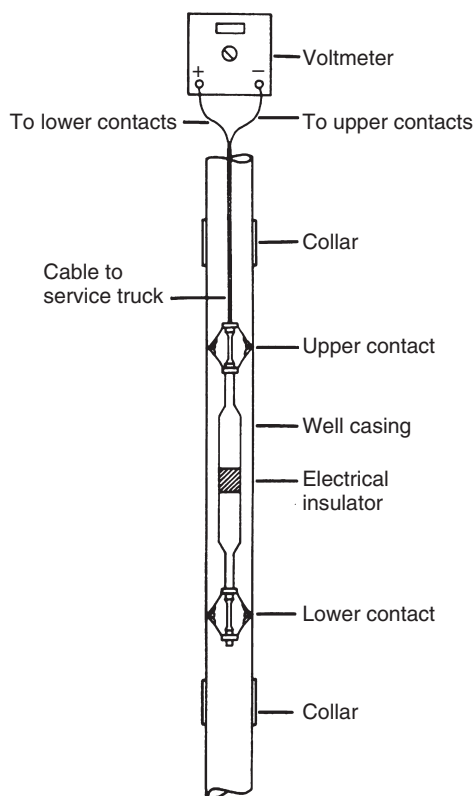
One of the concerns expressed about determining the required current for cathodic protection using the  $E \log i$  test is whether or not enough current reaches the bottom of the casing string. Casing potential profiles determined with interior inspection devices have confirmed that this method applies cathodic protection current to casing exteriors as deep as 3960 m (13,000 ft).<sup>54</sup> Figure 8.17 shows the instrument used for this casing potential profile test, and Figure 8.18 shows a typical casing potential profile. The unprotected profile shown in Figure 8.18 shows locations where corrosion is to be expected while the profile with cathodic protection current applied shows a steadily increasing potential from the bottom of the well indicating that the casing is protected from external corrosion. A significant drawback to the casing potential profile method of determining if cathodic protection is needed or effective is the need to shut down the well for the measurements. The lost production can be significant.

Galvanic anodes have been used for well casing cathodic protection, but the use of impressed current systems is more common. The design and location of ground bed and rectifier systems for well casings follows the general procedures for other cathodic protection systems. Particular attention should be paid to keeping all anodes at a sufficient distance from the nearest well casing to prevent stray current corrosion.<sup>54,56</sup>

**Capillary Tubing Corrosion** Capillary tubing is a very small diameter string of tubing usually run alongside the



**Figure 8.16**  $E \log i$  data for a well casing indicating the need for approximately 18 amps of applied cathodic protection current.<sup>58</sup>

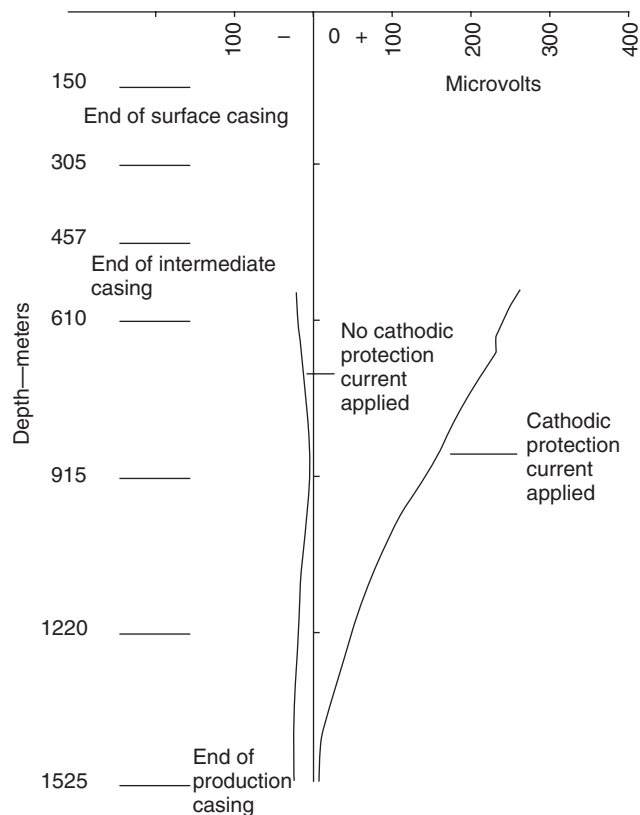


**Figure 8.17** Casing potential profile tool.<sup>58</sup> Reproduced with permission of NACE International.

outside of the production tubing and banded to the outside of the production tubing. It is common for this tubing to be made from CRAs, and the negligible galvanic effect due to contact with the production tubing is seldom a problem due to the lack of chemically reducible species in the casing-tubing annulus. Capillary tubing is used for a variety of purposes and is available in alloys ranging from austenitic stainless steel to high-nickel alloys. This tubing seldom has serious corrosion problems, and most alloys are  $H_2S$ ,  $CO_2$ , and chloride resistant to various degrees depending on temperature and other variables.

#### Inhibitors for Tubing and Casing in Production Wells

The use of corrosion inhibitors has been common in producing wells since the 1930s. It remains the most common means of corrosion control and is common in wells with carbon steel tubing. Wells finished with materials selected in accordance with MR0175/ISO15156 are not protected from weight loss corrosion. That standard only addresses materials selection for resistance to environmental cracking.



**Figure 8.18** Typical casing potential profile plot.<sup>58</sup> Reproduced with permission of NACE International.

Filming inhibitors are commonly used in flowing fluids. Chemical scavengers, for example, oxygen and  $H_2S$  scavengers, are used in confined spaces like casing-tubing annular spaces.

The temperature of production fluids is a major consideration in choosing corrosion inhibitors. Up to approximately  $65^\circ C$  ( $150^\circ F$ ) inhibitor treatment is routine. At higher temperatures up to approximately  $150^\circ C$  ( $300^\circ F$ ), extensive testing is necessary to identify appropriate inhibitors. It is possible to inhibit corrosion as high as  $220^\circ C$  ( $425^\circ F$ ), but these applications are questionable and are not generally accepted within the oilfield community.

In recent years, environmental limitations on discharge of inhibitor-containing waters have become important and have limited the choices of chemicals used and dosage limits. Corrosion inhibitors must also be compatible with other chemicals, for example, hydrate inhibitors.

Cleanliness is an important consideration in the use of corrosion inhibitors. Particles can clog injectors, and  $10\mu$  filters are often specified. Inhibitors are usually diluted in solvents—crude oil, hydrate inhibiting glycols,



and so on—and the injection of high volumes of solvent, which requires larger orifices to maintain higher flow rates, can tolerate larger particles suspended in inhibitor fluids. Clean surfaces also produce better corrosion inhibitor efficiency. With less surface areas for attachment, clean wells can be inhibited at lower inhibitor dosage rates. Periodic cleaning may lead to appreciable savings in overall inhibitor consumption, but this cleaning also means that inhibition dosage rates must be somewhat higher immediately after cleaning until the surfaces have been recoated with inhibitor films.<sup>33</sup>

Sand and other particles reduce the efficiency of filming inhibitors, because films will form on these solid surfaces.

**Gas Wells** Corrosion inhibitor treatments in gas wells can be fairly economical because they produce relatively small amounts of liquid requiring inhibitors. Gas phases are noncorrosive. The high fluid velocity in gas wells means that filming corrosion inhibitors must be resistant to high shear stresses.

While continuous treatment produces more reliable corrosion control results, most gas wells have batch treatment of corrosion inhibitors. Approximately 10 ppm of inhibitor in condensate phase can yield corrosion control, but in practice, the liquid production rate may not be known so it is common to use rules of thumb to estimate the required injection rate, for example, 1 pint/MMscf (14 L/million Sm<sup>3</sup>).<sup>59</sup>

Most batch treatments attempt to apply approximately 3–5 mils (75–125  $\mu$ ) of corrosion inhibitor, but the actual coverage will typically be only about one-tenth of the calculated coverage.<sup>59,60</sup>

Gas wells usually produce condensates in an annular dispersed pattern (Figure 5.41). The resultant mixing insures that corrosion inhibitors will be transported to tubing surfaces where they can adhere and provide corrosion protection.

**Oil Wells** Unlike gas wells, which are considered to be corrosive from the start of production, it is common practice to wait until oil wells start to corrode due to increased water cuts (Figure 3.1) before starting corrosion inhibition of wells and produced fluids. This approach has the disadvantage of starting corrosion control only after a predetermined amount of corrosion, for example, 10% wall loss, which means the tubing will have surface roughening and corrosion product buildup. Mechanical or chemical cleaning of the tubing interior then becomes advisable before starting inhibitor programs.<sup>33</sup>

The much higher volumes of liquid water produced in oil wells means that there are strong incentives to use the lowest possible effective doses of corrosion inhibi-

tors. Some low doses of corrosion inhibitors are more harmful than beneficial, and the users of these chemicals usually do not know the chemistry and operating principles of the commercial combined inhibitor packages.<sup>59</sup>

It is common to start with dosages in the 5–15 ppm range for water-soluble inhibitors and approximately 25 ppm for oil-soluble inhibitors based on calculated barrels of water per day produced. Adjustments are then made based on topside monitoring of corrosion rates with coupons or electrical resistance probes.

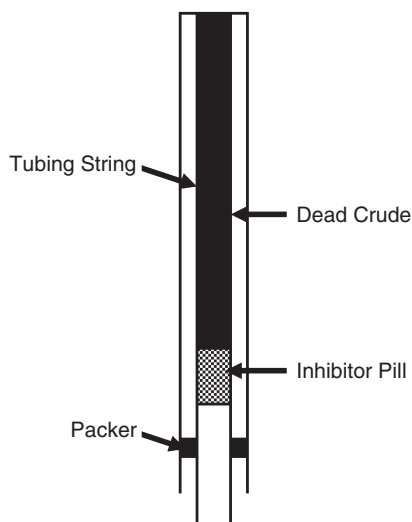
**Application Methods** Virtually all authorities claim that continuous injection is the most efficient way in corrosion inhibitor application, but the special equipment needs for continuous injection downhole mean that batch treatments are more common for production wells.

Batch treatments are most effective for gas wells. All methods require that producing wells be shut in for periods of up to 1 day depending on the depth of the well and the method used. The three common methods of batch treating wells are:

- Batch and fall
- Tubing displacement
- Squeeze treatments

The batch and fall method is used when gas wells are confirmed to be corroding. The well must have low liquid levels and sufficient natural bottomhole pressure to return the well to operation once the treatment is completed. Diluted liquid inhibitor is injected into the shut-in well and is allowed to fall through the tubing for approximately 6 h. The well is then returned to service and the natural turbulence of the produced gas stream distributes the corrosion inhibitor to the tubing walls. This method is relatively simple but does not work well in deviated wells, some of which may have locations where the well slope is not steep enough to deliver the inhibitor to the bottom of the well.

The tubing displacement method works for both oil and gas wells. The well is shut in and the liquid corrosion inhibitor “pill” of diluted inhibitor in a liquid carrier is placed in the well as shown in Figure 8.19. The well is back pressured to force the pill to the bottom of the well using crude oil, nitrogen, or natural gas. Gas is used to back pressure the well if the well will not produce with a full head of liquid. Once the well is returned to service, the concentrated inhibitor is diluted by the produced fluid and forms protective films on the tubing wall. The inhibitor film is diluted to spread the inhibitor and increase the likelihood of contact with all surfaces, but



**Figure 8.19** Tubing displacement method of lining production tubing with corrosion inhibitor.

it should not be diluted to less than 1000 ppm (0.1%). The time to place the pill at the bottom of the well is typically around 6 h, and this procedure is repeated at planned intervals, varying from every 2 weeks to quarterly.<sup>59</sup>

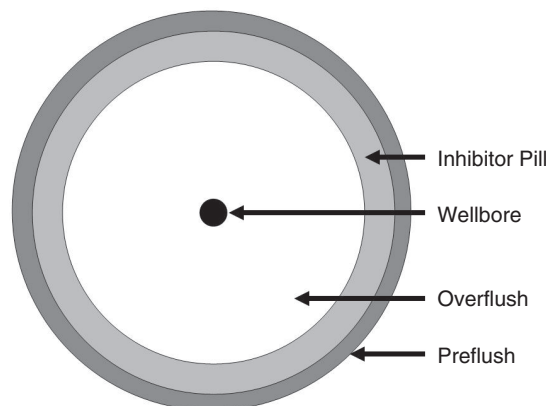
Squeeze treatments are similar to tubing displacement treatments, but the inhibitor pill is displaced beyond the bottom of the well and out into the formation (Figure 8.20). The liquid forcing the inhibitor into the formation is usually filtered-produced water, which replicates the formation water chemistry. An alternative is to use fresh water with from 2% to 3% potassium chloride added to minimize any clay swelling in the formation. If low formation pressures are a concern, then gas, diesel, or condensate may be used to displace the inhibitor pill into the producing formation.

The inhibitor is allowed to soak into the formation before returning the well to operation. This “soak in” time may be up to 48 h.

During all forms of batch treatment, the elastomeric seals at the bottom of the well are exposed to high concentrations of the inhibitor and the carrier solvent. Once wells are returned to service, the inhibitor concentrations remain high for several weeks. The effects of these concentrated chemicals on the sealing materials in use should be evaluated before starting batch treatments.<sup>61</sup>

Concentrated inhibitor solutions returned into the produced fluids by batch treatments can cause problems in topside processing equipment. Their compatibility with existing process operations must also be checked.<sup>59</sup>

Continuous inhibitor injection to downhole well locations can be by the use of capillary tubing or by



**Figure 8.20** Diagram showing location of corrosion inhibitor in formation after squeeze treatment.

insertion through the annulus. Either method requires specialized downhole equipment that must be installed during initial installation in the well or during extensive workovers.

Dedicated capillary tubing, usually strapped to the outside of the production tubing, is perhaps the most reliable means of inserting corrosion inhibitors into the produced fluid stream. But this method is not popular with production engineers because this makes the production tubing string, with the attached capillary tubing, harder to place and remove. It slows workovers and other operations.<sup>59</sup>

The alternative to continuous injection through capillary tubing is to fill the annulus with the corrosion inhibitor. This method is sometimes used when large volumes of chemicals must be injected into the production stream, for example, if corrosion inhibitor and hydrate inhibitors are both being injected into the downhole fluids.

This method requires a clean annulus, and, if the injection rate is too slow, the inhibitor may lose effectiveness due to overheating in the annulus before it is injected. The method is most often used on oil wells with artificial gas lift. The pressure valve in a side pocket mandrel opens and inserts inhibitor into the production stream. Intervals between injections can be as long as several hours. Disadvantages of this method include the fact that the inhibitor must be persistent and protect the tubing until the next injection of inhibitor and high instantaneous concentrations of inhibitor may need to be handled in downstream processing facilities.<sup>59</sup>

Valves for both methods of continuous inhibitor injection are prone to sticking and plugging.

Table 8.4 is a summary of the various inhibitor treatment methods and practices for producing oil and gas wells for one operator in the Gulf of Mexico. Tubing displacement is probably the most common method of corrosion inhibition because it has the fewest equipment requirements and drawbacks.

The economics of using corrosion inhibitors for production well corrosion control depends on the method of inhibitor application. The annual cost of corrosion inhibitors for one well is typically in the thousands of dollars. Continuous inhibitor injection systems cost in the tens of thousands of dollars. The biggest costs are for injection tubing and the increased costs of more complex and time-consuming workovers. For batch treatments, the largest cost is the lost production during downtime for injection.<sup>59</sup>

The use of corrosion inhibitors for downhole corrosion control has been standard practice for many years, and most wells currently in production use this approach. The complexity of continuous injection and the lost production revenue associated with shutdowns for batch injection have led many operators to decide to use CRAs, usually 13Cr, on most new well completions.<sup>59</sup> The conversion to 13Cr martensitic stainless steels is appropriate, because any fluid conditions that would

preclude the use of this series of CRA would also be so aggressive that corrosion inhibitors would not work and more CRAs would become necessary. One alternative to this approach is the use of internally coated tubing, which is discussed in the next section.

### Internally Coated Tubing for Oilfield Wells

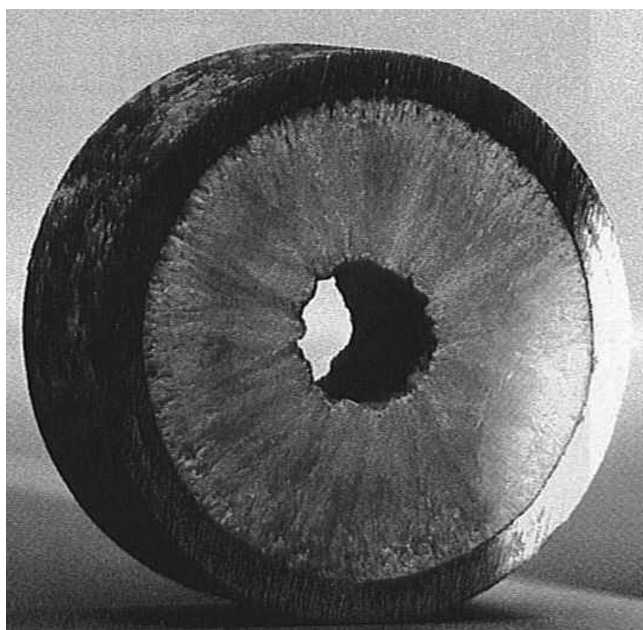
Internal coatings are often used on water injection wells as an economical means of enhanced corrosion control for low-cost carbon steel tubing. As discussed earlier in this chapter in the section on injection wells, the primary means of corrosion control for these wells is by the use of oxygen scavengers to minimize the corrosivity of the injection water. As an added means of corrosion control, it is common to use internally coated injection tubing for those wells that cannot use fiber-reinforced tubing. The usual reasons for using steel pipe are pipe diameter, fluid pressure, and the length of the injection tubing string. Internal coatings are also used on production tubing, both as a means of corrosion control and to reduce friction and increase flow rates.<sup>59</sup> The smoother surfaces of internally coated or lined tubing also reduce paraffin buildup and scale deposits. (Figure 8.21).

**TABLE 8.4 Corrosion Inhibitor Treatment Methods for Producing Oil and Gas Wells**

Method (Frequency)	Basic Description	Applications	Disadvantages	Additional Comments
Batch and fall (monthly)	Shut in, pump into tubing, allow to fall	Gas wells	Cannot treat below liquid level	Wells >1000 psi, rate of fall depends on gas density
Tubing displacement (quarterly)	Shut in, pump full tubing displacement minus safety factor	Use full volume diluted chemical or slug displaced with diesel, crude oil, water, or nitrogen	Overdisplacement can damage formation	Requires reservoir and subsurface evaluation to identify wells that can have displacement treatment
Squeeze (monthly or semianually)	Similar to displacement, chemicals forced into reservoir	Chemical returns into produced fluid from reservoir storage	High risk of formation damage	Not normally recommended due to risk of formation damage
Gas lift (continuous)	Pump small volume of chemical into gas-lift gas at wellhead continuously	Gas-lift wells only		
Downhole injection (continuous)	Chemical injection lines	Any new well that chemical injection lines can have installed	Plugging potential, initial capital cost	Injection valves adjusted to control injection rate
Dump bail	Use wireline bailer to spot chemical to location in well	May need several trips to deliver sufficient inhibitor using concentrated products	Mechanical risk	Aluminum bailers do not hold much chemical volume

**Internal Coating Systems for Tubing in Wells** There are a variety of coating systems available for tubing lining. Table 8.5 summarizes the relative cost of the resins. While cost is a consideration in resin selection, the maximum temperature that the tubing will see in downhole service is often the deciding factor in determining which resin system should be used. Maximum service temperatures are in the range of 120°C (250°F) to 150°C (300°F).<sup>62,63</sup>

**Problems with Internally Coated Tubing** Problems with internally coated tubing include wireline damage, deformation and cracking of coatings due to mechanical loads, and debonding of coatings due to sudden pressure releases.



**Figure 8.21** Paraffin deposits on the inside of Gulf of Mexico production tubing.

Wireline damage in tubing is similar to the damage shown for drill pipe in Figure 8.7. The damage is most likely to occur at joints and can be minimized by slow wireline speeds (<0.5 m/s or <100 ft/min). Downhole tools should be plastic coated, and wheeled centralizers or guides that keep the wireline near the center of the tubing also help. Corrosion inhibitor applications should be reintroduced immediately after running wirelines in order to refilm any exposed metal surfaces.<sup>62,63</sup>

Rounded tubing connectors minimize stress concentrations that can lead to cracking. Of course these premium connectors cost extra.

Another problem associated with lined or internally coated tubing is rapid pressure release. All organic coatings are permeable to moisture and gases, and sudden pressure releases can lead to debonding as shown in Figures 6.23 and 6.25.

**Concluding Remarks about Internally Coated Tubing** Coatings are imperfect means of corrosion control and must be supplemented by inhibitors of some sort. For water injection wells, the inhibition is usually by the use of oxygen scavenging after some other means of deaerating the water. For production wells, most common corrosion inhibitor packages rely on thin film formation of some sort of organic molecules attached to the surface.

International organizations have developed standard and guidance on internal coatings and lining to include the following NACE publications:<sup>64-70</sup>

- NACE SP0181, Liquid-Applied Internal Protective Coatings for Oilfield Production Equipment
- NACE RP0188, Discontinuity (Holiday) Testing of Protective Coatings on Conductive Substrates
- NACE RP0191, Application of Internal Plastic Coatings for Oilfield Tubular Goods and Accessories

**TABLE 8.5** Relative Costs of Resin Materials Used as Tubing Coatings and Liners

Material	Abbreviation	Relative Cost
Polyethylene	PE	1
Polypropylene	PP	1.1
Polyamide (nylon) 11	PA11	6
Polyketone	PK	5
Polyvinylidene fluoride	PVDF	15
Polytetrafluoroethylene	TFE	50
Fluorinated ethylene propylene copolymer	FEP	65
Ethylene—tetrafluoroethylene copolymer	ETFE	65
Chlorotrifluoroethylene—ethylene copolymer	ECTFE	65



- NACE RP 0291, Care, Handling, and Installation of Internally Plastic-Coated Oilfield Tubular Goods and Accessories
- NACE TM0183, Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods in an Aqueous Flowing Environment
- NACE TM187, Evaluating Elastomeric Materials in Sour Gas Environments
- NACE TM 0192, Evaluating Elastomeric Materials in Carbon Dioxide Decompression Environments

### Material and Corrosion Concerns with Artificial Lift Systems

Natural gas and most new oil wells flow due to downhole formation pressure. As oil wells age, it usually becomes necessary to add some form of artificial lift system, pumps, or other devices designed to bring the liquid crude oil to the surface. There are several options including:

- Beam-pumped wells
- Gas-lift systems
- Hydraulic lift systems
- Electrical submersible pumps (ESPs)
- Progressive cavity pumps

Each of these methods has unique materials and corrosion requirements. Most oil wells have some sort of artificial lift. Beam-pumped wells are the most common for onshore applications and ESP pumps are most common in offshore locations where their reduced topside weight and increased flow capacity are important. Most operators try to stay “pumped off,” maintaining a minimum liquid level over the pump intake. This results in little liquid in the annulus, and most of the liquid in the annulus will be oil which produces hydrocarbon condensation of the annulus interior with  $\text{CO}_2$  or  $\text{H}_2\text{S}$  in the water, which tends to remain below the oil in the annulus.<sup>20</sup>

CRA's are used for many components of artificial lift systems. This seldom creates galvanic corrosion problems with carbon steel and other alloys downhole, because the level of reducible chemicals (oxygen, hydrogen ions, etc.) is very low. At the worst, the corrosion rate on the larger carbon steel components will be twice the rate if no CRA cathodes were present, because the large anode sizes tend to reduce any effect of galvanic coupling.<sup>71</sup>

**Beam-Pumped Wells** Figure 8.22 shows the topside components of a beam-pumped well. The moving head of the well assembly causes a long string of sucker rods



**Figure 8.22** Topside of a beam pumping unit.

to move up and down inside the well. A chrome-plated polished rod on the surface passes through an elastomeric-sealed stuffing box and is connected to a long series of sucker rods that are strung inside the tubing to the bottom of the well. At the bottom of the well, a downhole pump moves the liquid oil and produced water up the tubing string. As downhole pressure decreases, gas breakout will occur, and gas is usually removed from the tubing near the surface. Figure 8.23 is a drawing of a beam-pumping system. These systems are commonly used on low-volume onshore wells. It is not uncommon to see hundreds of the pumping jacks shown in Figure 8.22 in an oil field that may be several decades old but still economically productive.

The most common form of materials failure is corrosion fatigue of the sucker rods, long rods, usually of carbon or low-alloy steel (e.g., UNS G41420—AISI 4142 alloy), with upset ends that are formed and machined for connecting to other rods. This tends to occur at the upset ends where stresses are the greatest (Figure 5.64). Pitting corrosion (Figure 5.66) can produce stress risers that lead to corrosion fatigue cracks.

Sucker rods should be full-length normalized after quenching and tempering to eliminate undesired differences in microstructure and mechanical properties near the upset ends. Rods are commonly supplied in 25 ft (7.62 m) and 30 ft (9.14 m) lengths with diameters from 5/8 in. (15.88 mm) to 1 1/8 in. (28.58 mm). Their relative length to diameter means that they are flexible and can bend around some high-radius downhole tubing bends.

Another sucker rod failure mode is wear, which is most likely to occur near the midpoint of the rods at locations where the well deviates from horizontal. Factory-installed sucker rod guides, made from

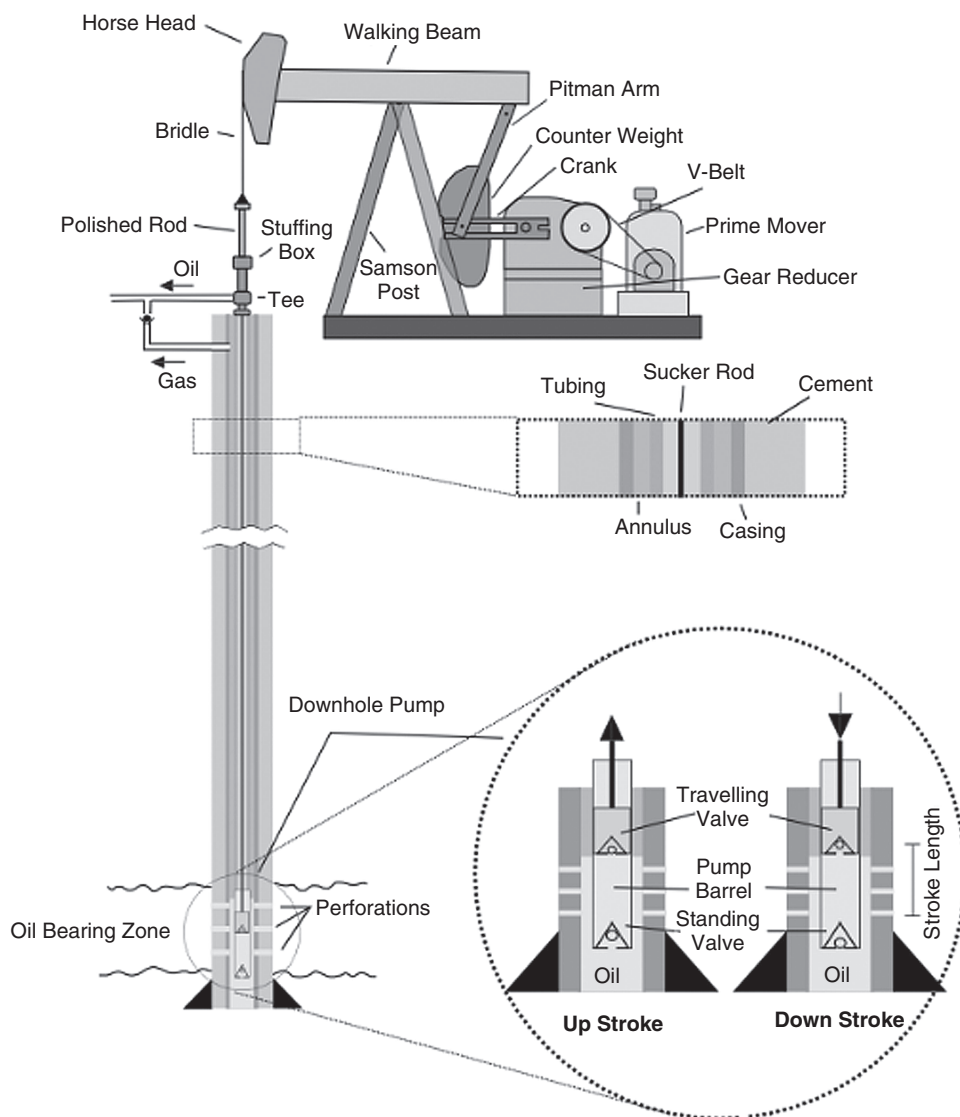


Figure 8.23 Beam-pumped well diagram.

abrasion-resistant injection-molded polymers, are installed along the rod at selected locations. Up to three guides per rod are sometimes installed. These guides also reduce wear on downhole tubing, which is softer than the rod metal and is more likely to wear leading to leaks.

Most sucker rods are made from heat-treated low-alloy steel. Titanium, aluminum, and fiberglass sucker rods are available. The primary advantage claimed for these materials is their increased strength-to-weight ratios compared to steel. While these materials have been available for many years, low-alloy steel sucker rods are usually used.

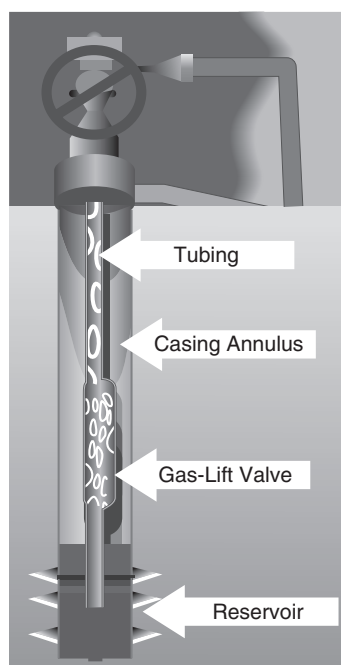
Corrosion of sucker rod strings sometimes occurs near the wellhead. This is usually due to air leaking in at the polished rod-stuffing box seal. The most common means of preventing this corrosion is by maintaining a

positive pressure on the downhole tubing, insuring that any gas leakage is from inside the well to the atmosphere.<sup>59</sup> The deep mesa-type pitting corrosion shown in Figure 5.66 was due to high concentrations of  $\text{CO}_2$  in the produced fluids. The 9-chrome material in use at the time proved inadequate for corrosive conditions, and 9-chrome alloys are no longer common for downhole applications.

Corrosion and wear of downhole pumps is controlled by the use of appropriate alloys.<sup>33</sup>

A number of industry standards are available on the manufacture, care, and testing of sucker rods.<sup>72-74</sup>

**Gas-Lifted Oil Wells** These wells usually have packers, and if the lift gas is corrosive due to the presence of oxygen, moisture, or corrosive gases (e.g.,  $\text{CO}_2$  or  $\text{H}_2\text{S}$



**Figure 8.24** Gas-lifted oil well.

from unprocessed natural gas), corrosion can occur in the annular spaces.

Lift gas is usually transported downhole in the annulus, and one of two types of valves are installed downhole to inject the gas into the production string. (Figure 8.24) Conventional gas-lift valves are installed as the tubing is placed in the well and must be removed with the tubing string. Side-pocket mandrels allow the installation and removal of valves by wireline while the mandrel remains in the well, eliminating the need to pull tubing for repair or replacement of valves.

Corrosion problems in gas-lifted wells may be due to wet lift gas or the absence of packers. Corrosive lift gas causes problems in the annulus as well as on tubing interiors. It is not uncommon for lift gas to be more corrosive than produced reservoir gas, which is sometimes reinserted as lift gas.

Corrosion control is achieved in gas-lifted wells through the use of noncorrosive lift gas and by the use of internal production tubing coatings, CRA tubing strings, and/or the use of filming corrosion inhibitors.<sup>20</sup>

**ESPs** These pumps, which are the most common oil well pumps for offshore use, have few corrosion problems. The pumps themselves are available in a variety of CRAs, and the electric power cables, which usually run in the annulus, have CRA (often nickel-based) cable sheaths. Metallic sheathing is necessary, because all polymers used for electrical insulation are permeable

to gases, and corrosive gases, for example,  $\text{CO}_2$  or  $\text{H}_2\text{S}$ , could cause corrosion of the copper power wire. The downhole components of these pumps are made from materials that can withstand downhole temperatures of up to  $150^\circ\text{C}$  ( $300^\circ\text{F}$ ) and the associated high-pressure chemistries of the produced fluids. They lose efficiency with downhole gas contents greater than approximately 10%. Improved versions of these pumps are available with downhole gas separators that can remove gases and transport them to the surface in parallel tubing strings.

ESPs have tight dimensional tolerances and can have erosion and wear problems when producing sand.

**Hydraulic Lift Systems** These systems get power from high-pressure liquids injected into the tubing that transports the high-pressure liquid to the bottom of the well. The downhole assemblies then transmit energy to the produced fluid, which is usually produced through the annulus. Downhole equipment can be either jet pumps (injecting the higher-pressure lift liquids into the production tubing using Venturi jet pumps with no moving parts) or reciprocating piston pumps to force produced fluids to the surface. Hydraulic lift fluids are either reinjected crude oil or produced water. If produced water is reinjected, it may be corrosive if it has been contaminated at the surface by oxygen-containing air. This corrosion is controlled by the use of corrosion inhibitors, including oxygen scavengers and film-forming inhibitors.

Venturi systems can be used in deviated wells where beam-pumped sucker rods or other mechanical systems will not work. Reciprocating piston pumps can operate until well depletion and handle low production rate wells. Either type of pumping system can also deliver chemicals, for example, corrosion, paraffin, or emulsion inhibitors, to the produced fluid.

Drawbacks to hydraulic lift systems include their high energy consumption and relatively high cost. The use of coiled tubing to deliver hydraulic fluids downhole has reduced costs and has enabled their use in additional wells.

**Progressive Cavity Pumps** The moving parts of progressive cavity pumps that are exposed to production fluids are the helical screw rotor and drive shaft, which are usually chromium hard-faced (thicker than electrolytic chrome plating) heat-treatable carbon or low-alloy steels, and the stator, made from a chemically resistant hard elastomer. (Figure 8.25).

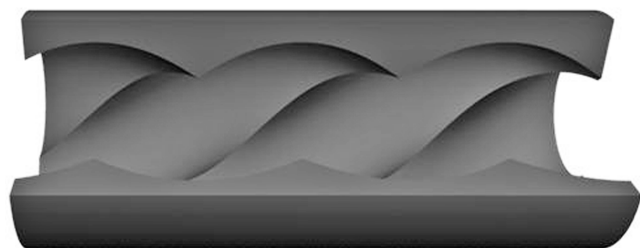
Problems with helical screws and drive shafts seldom occur. Stators are the components most likely to degrade and need replacement. Properly chosen materials should last 3–5 years, and most of the metallic components of

the pump can be reused or refurbished after the elastomeric stator is replaced.<sup>1</sup>

Friction between the stator and the rotor raises the temperature of both components above the downhole fluid/formation temperature. Candidate stator materials should be tested for fluid compatibility using established standards which measure swelling resistance, changes in hardness, and other parameters associated with the exposure of polymeric materials to downhole fluids at the estimated temperature of the operating pump.<sup>69,70</sup> Table 8.6 presents the elastomeric materials most likely to be available for downhole progressive cavity pumps. The table only shows generic classifications of the main resin components, and all commercial elastomers will have minor constituents that affect their chemical and wear resistance. This is why fluid compatibility testing is recommended for any large-scale application, for example, use in a major new field.

### Wellheads, Christmas Trees, and Related Equipment

Wellheads are the components at the top of a well that provide structural and pressure-containing support for the drilling and production equipment. The primary



**Figure 8.25** Cross-section view of an elastomeric stator for a progressive cavity pump. Stators for oil wells usually have longer stators (more turns) because of relatively high downhole pressures.

purposes of wellheads are to provide suspension points for downhole equipment and pressure seals for the tubing and casing strings running from the bottom of the hole.

After completions are finished, Christmas trees are attached to most wells. “Trees” are assemblies of valves, chokes, spools, and other fittings used to control flow of fluids and equipment into and out of the well. Figure 8.26 shows a Christmas tree attached to a wellhead on an offshore production platform in the Gulf of Mexico. Some Christmas trees are more complex. Subsea Christmas trees, which must operate for many years with no inspection or maintenance, are often machined from a single block of metal instead of being bolted together with flange connections.<sup>75</sup>



**Figure 8.26** Christmas tree attached to a wellhead.

**TABLE 8.6 General Elastomer Selection Guide for Progressive Cavity Pumps**

Characteristics	Elastomer Type			
	Buna	High Nitrile	Hydrogenated	Fluoroelastomers <sup>a</sup>
Mechanical properties	Excellent	Good	Good	Poor
Abrasion resistance	Very good	Good	Good	Poor
Aromatic resistance	Good	Very good	Good	Excellent
H <sub>2</sub> S resistance	Good	Good	Excellent	Excellent
Water resistance	Very good	Good	Excellent	Excellent
Temperature limit <sup>b</sup>	95°C (200°F)	95°C (200°F)	135°C (275°F)	150°C (300°F)

<sup>a</sup> Common trade names for fluoroelastomers include Viton, Hyflon, Halar, and Teflon.

<sup>b</sup> The internal operating temperature of pumps may be significantly higher than the reservoir fluid temperature due to friction between rotors and elastomeric stators.



Wellheads, which support downhole tubing, casing, and other components, are connected at the top of wells to Christmas trees, which control production rates and fluid flows out of the well and may also direct fluids and equipment into the well. The primary material considerations for wellheads are strength, erosion resistance, and corrosion resistance. The relatively small size of wellhead and Christmas tree equipment compared to tubing, casing, pipelines, and so on means that materials costs are secondary considerations. It is common to use whatever material is necessary to insure reliable production and minimal maintenance for wellhead components.

Christmas trees, which regulate flow rates and also change the primary direction of flow from vertical to horizontal, have fewer strength requirements, because they are not limited by downhole space limitations. The requirements for pressure containment suggest the use of low-alloy heat-treatable steels for the bodies of these components. Lining the fluid-exposed surfaces with hard, erosion-corrosion resistant alloys provides the necessary environmental resistance, but all components must be made from H<sub>2</sub>S-resistant alloys, because no coating or hard facing is without defects that can allow gas penetration. While a composite structure of high-strength steel with erosion-corrosion lining is possible for the main components, the smaller internal components (gates, springs, etc.) are not coated and are made from erosion-corrosion resistant alloys. Figure 8.27 shows erosion on a Christmas tree gate valve. The use of hard corrosion-resistant materials and control of production to fluid flow rates that minimize erosion are means of controlling this erosion. The use of company



**Figure 8.27** Erosion of a gate valve component producing loss of a sealing surface. Photo courtesy of NACE International.

guidelines has largely replaced API RP14E erosion recommendations for this application, because many companies find the API guidelines to be overly conservative. This leads to perceived unnecessary reductions in production rates. The economic consequences of reduced production rates must be balanced against the costs of production shutdowns and possible reduced reliability.

Production wellheads have a variety of high-strength components necessary to support the weight of the casing and tubing. This places major limitations on the type of materials that can be used. The restrictions of NACE 0175/ISO 15156 usually determine which materials can be used except in the most benign onshore applications.<sup>16,34,35</sup> API Spec 6A prescribes strength and impact properties for wellhead materials. Required strength levels depend on the pressure ratings of the equipment, for example, equipment utilized to 10,000 psi (69 MPa) must be made from materials having a minimum yield strength of 60,000 psi (414 MPa), and higher pressure equipment must be made from materials using materials with a specified minimum yield strength of 75,000 psi (517 MPa). Hardness levels and Charpy impact properties are also specified.<sup>76</sup> Other similar specifications cover subsea wellheads and Christmas trees.<sup>77</sup> The ISO standard for wellheads and Christmas trees is slightly different.<sup>78</sup>

The wellhead and Christmas tree standards also specify various classes of service depending on pressure, corrosivity, and temperature. It is common for suppliers to supply valves with different materials selected for:

- Body and bonnets
- Flanges
- Wetted internals
- Valve stems
- Various types of seals
- Trim components including both wear and nonwear components

Valves are supplied depending on different API or ISO service classifications, which vary depending on pressure, corrosivity of the internal environment, and temperature.

Charpy impact toughness requirements in API specifications are intended to minimize brittle behavior. Many wellhead and Christmas tree components are massive pieces of metal that are heat treated after forming, usually by forging. If the heat treatment is not correct, then brittle fracture can result.<sup>79</sup> Installations of subsea completions, and the tremendous expenses associated with their retrieval, maintenance, or repair, mean that subsea wellheads and Christmas trees are now intended to last for the life of the producing well. This

can be 30 years or longer with no anticipated inspection, maintenance, or parts replacement. The tremendous expenses associated with subsea completions means that materials selection and fabrication must be as careful and reliable as possible.<sup>75</sup>

Springs in Christmas trees present difficult materials selection and fabrication choices. Most springs must have very high strength and hardness to work effectively. High strength and hardness makes them susceptible to chloride stress corrosion cracking (SCC) and H<sub>2</sub>S, and not in compliance with the requirements of NACE MR0175/ISO 15156. The acceptable high-strength alloys for this service are cobalt alloys, which are allowed to HRC 55 or 60 depending on the alloy, and precipitation-hardened nickel-based alloys that can be used to a maximum hardness of HRC 50.<sup>35</sup>

## FACILITIES AND SURFACE EQUIPMENT

Topside equipment and surface facilities are much more likely to have corrosion problems than downhole wells and wellheads. This is because they are exposed to air, and any air leaking into fluids can cause internal corrosion as well as atmospheric corrosion of the equipment exteriors.

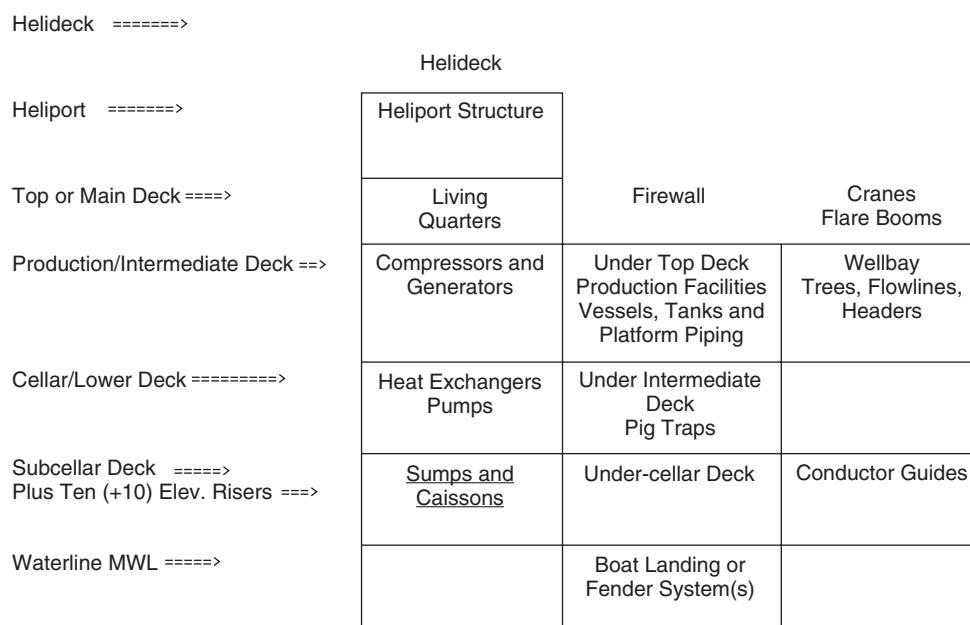
Figure 8.28 shows a typical arrangement of topside equipment for a medium-sized offshore platform in the Gulf of Mexico. Most of the process equipment is listed by category in the labels associated with the various bays of the structures.

NACE Report 1F192 discusses a number of alloys for a variety of downhole and topside applications.<sup>80</sup> This is one of a number of international guidelines on the use of CRAs in oilfield applications.

## Piping

Most topside corrosion problems are associated with piping systems. Carbon steel is used for most piping because it is inexpensive and has few internal corrosion problems in hydrocarbon systems. Other materials are used for corrosive environments, and this includes the use of CRAs for some hydrocarbon systems, for example, if they are necessary due to high levels of CO<sub>2</sub> or H<sub>2</sub>S, usually in gas-handling lines. The alloy classifications in NACE MR0175/ISO15156 provide a list of possible alloys for this use. While the standard is only intended to describe the alloys acceptable for H<sub>2</sub>S service, piping systems should always be made from these alloys with the final selection depending on weight loss or other corrosion resistance. Further guidance is available in NACE Report 1F192.<sup>80</sup> While this report discusses a number of internally clad piping systems (CRA lining of carbon steel piping), several organizations have reported debonding problems with this piping, and the use of internally clad piping is considered questionable by many authorities.

Titanium can be used in seawater and other systems with fluid velocities as high as 7.6 m/s (25 ft/s). Seawater velocity needs to be greater than 1.2 m/s (4 ft/s) to avoid biofouling.



**Figure 8.28** Typical arrangement of topside equipment on an offshore platform. MWL, mean water line.

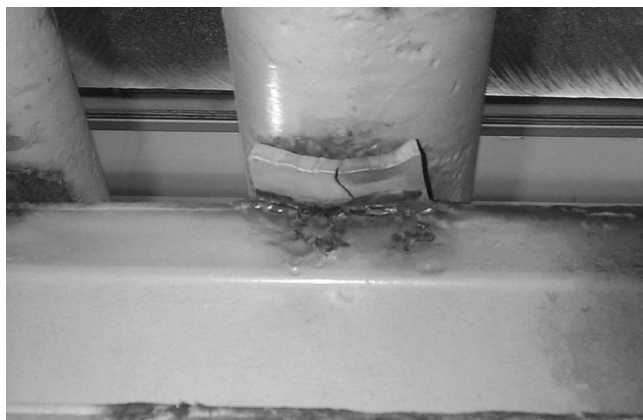
Copper-based alloys (usually 90/10 copper nickel or 70/30 copper nickel) are used in seawater handling systems, fire suppression piping, and so on. The liquid velocity limits for copper-based piping depend on size and vary from 3.5 m/s (11.5 ft/s) for 10 cm (4 in.) cupro-nickel piping to lower levels for other copper alloys.<sup>81</sup>

It is important to keep the piping system design as simple as possible with limited deadlegs and other locations where deposits can accumulate and lead to corrosion. It is also important to insure inspectability and provide for extra tie-ins so that designs can be altered as necessary.

Fiberglass-reinforced plastic (FRP) piping is sometimes used for water and other systems. Problems associated with this piping are generally due to the increased support structures necessary for this piping. Other problems have been reported with joining the piping. A major advantage of the piping is the smooth interior surfaces which limit fouling attachment sites. This has led to the increased use of FRP piping for fire suppression systems.

Figure 8.29 shows corrosion of a carbon steel pipe protected from abrasion by a neoprene gasket. Unfortunately, the neoprene collects moisture, and the external pipe coating is not an immersion coating. Figure 8.30 shows a better approach to piping supports. A round U-bolt with a plastic sleeve holds the pipe against a non-absorbent plastic half-round. Several suppliers of this kind of piping attachments are commercially available.

Thermal expansion and contraction can be a major problem in piping systems. The vertical expansion loop shown in Figure 3.12 should normally be avoided. This loop on a steam injection line can lead to slugging when condensate builds up in the upstream portion of the loop. Most authorities would recommend horizontal expansion loops whenever possible.



**Figure 8.29** Corrosion of pipe at neoprene support gasket.

**Firewater Systems** Firewater lines are stagnant except during monthly testing, so it is generally acceptable to use carbon steel, which corrodes for a small number of days after the testing until the dissolved oxygen in the water is used up. This intermittent service is much less corrosive than constant use. Other materials used for this piping include cupronickels, PVC, and austenitic stainless steel. Unfortunately, all metallic firewater lines are subject to underdeposit corrosion due to biofouling or debris. This was shown in Figure 4.31, which shows corrosion at the 6 o'clock position in a copper-nickel firewater line from a Gulf of Mexico platform.

Many companies use FRP for this service, because metallic corrosion products can clog nozzles. FRP also has smooth surfaces and is less likely to promote biofouling communities. API RP14G, Fire Prevention and Control, lists FRP as one of the acceptable piping options.<sup>82</sup>

Most firewater systems are “wet” systems with water in all lines at all times. In cold climates, this can become an icing problem, and dry systems must be used. Unfortunately, “dry” systems can often have water trapped at valves and low spots in the piping system, leading to corrosion like that shown in Figure 8.31. Dry systems require frequent maintenance and inspection, drying with inerting gases, and so on.

**Seawater Systems** Seawater lines are often titanium or cupronickel to minimize corrosion.

Pumps often have nickel-aluminum bronze (NAB) housings, pump bodies, shafts, and fasteners. Selective phase attack of some NAB components is possible, but this problem, which is due to improper foundry practice, is relatively rare.

Cast stainless steel may be cheaper, but it is usually not as strong or cavitation resistant. Stainless steel shafts



**Figure 8.30** Insulated U-bolt assembly to avoid corrosion at pipe support.



**Figure 8.31** Corrosion at a control valve in a “dry” fire sprinkler system. Photo courtesy of Mark Hopkins, Hughes Associates, Baltimore, MD.

can also develop pitting or crevice corrosion in gland areas during shutdowns. Very large pumps may have cast iron bodies with CRA impellers. This leads to some galvanic corrosion, but the relatively large size of the cast iron body minimizes the problem.

**Water Handling and Injection Equipment** Table 8.7 summarizes corrosion problems and control methods for oilfield water handling systems.

NACE SP0499 cites NORSOK guidance for injection water based on dissolved oxygen equivalents of:

Oxygen equivalent = ppb oxygen + 0.3 ppb free chlorine

For conditions where the oxygen equivalents are:

50 ppb for 90% of operation time; and

200 ppb for 10% of operation time, noncontinuous

**TABLE 8.7 Internal Corrosion and Corrosion Control of Water Handling and Injection Equipment<sup>20</sup>**

System or Equipment (Environment)	Usual Problem Areas	Evaluation Methods (Detection and Monitoring)	Most Common Corrosion Control Methods
Vessels and tanks	Shell when water very corrosive Bottom under deposits Vapor space when sour	Inspections Failure history Coupons, probes Occasionally iron content and/or bacterial activity Galvanic probes (oxygen detection)	Oxygen-free operation (exclusion and/or removal) Cathodic protection (CP) Coatings Periodic cleanout Occasionally: biocides or inhibitors Nonmetals—if air intrusion is tolerable
Filters	Connections when bimetallic At filter media (sand) level	Same as vessels	Same as vessels
Gathering and injection lines and plant piping	Along bottom under deposits	Same as vessels	Oxygen-free operation Coatings and linings (including cement)  Periodic line pigging Occasionally: biocides or inhibitors
Injection and transfer pumps	All wetted parts  Seals leaking air	Failure history  Inspection Galvanic probe (oxygen detector)	Oxygen-free operation  Metallurgy
Injection wells	Tubing interior, inhole valves, fittings, etc. Wellhead and Christmas tree Annulus above packer (depends on packer fluid)	Failure history Coupons Occasionally iron content and/or bacterial activity Galvanic probes (oxygen detection)	Oxygen-free operation Coatings and linings Occasionally biocides or inhibitors

Source: Information from H. Byars, *Corrosion Control in Petroleum Production*, 2nd ed., NACE International, 1999, Appendix 1A, pp. 18–22.



and the temperature is 30°C (86°F) or less, NORSOK recommendations in Table 8.8 are suggested.<sup>83</sup>

### Storage Tanks

Most of this discussion will deal with above-ground storage tanks (ASTs), which are much more common in oil and gas production than the usually smaller, underground storage tanks (USTs). Protective coatings supplemented by cathodic protection are used for external corrosion of USTs, and these tanks present few unique problems.

Figure 8.32 shows the exterior of the same AST shown in Figure 6.18. Exterior corrosion of the air-exposed portions of ASTs is controlled by the use of

protective coatings and seldom presents unique challenges. The exterior surfaces have relatively simple geometries and, if properly coated, may perform well for many years. Maintenance and safety concerns are associated with personnel ladders, floating roofs, and other attachments.

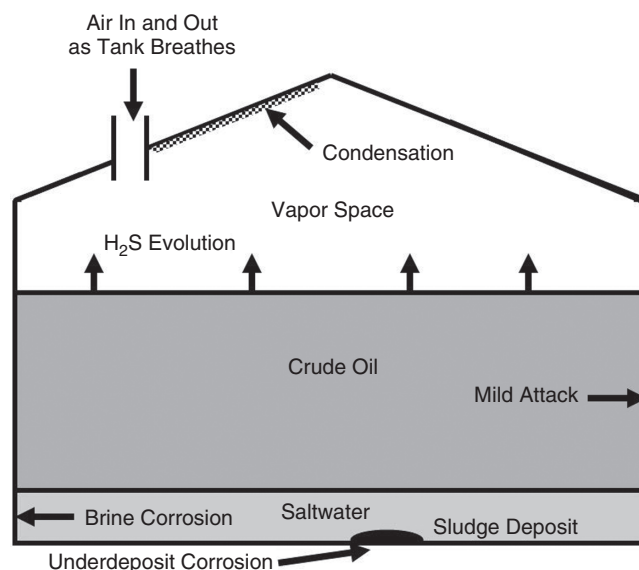
Figure 8.33 shows the locations on a crude oil AST where corrosion is likely. Little corrosion is expected on the interior walls of the tank where metal surfaces will be hydrocarbon wetted. Corrosion problems occur in the vapor space above the stored liquid and at the bottom of the tank, where water and sludge deposits may accumulate. ASTs of this general design may store over half a million barrels of liquid product. Many problems associated with these large tanks are due to their

**TABLE 8.8 NORSOK Recommendations for Injection System Materials<sup>83</sup>**

Injection Water	Tubing and Liner	Completion Equipment (When Different from Tubing/Liner)
Deaerated seawater	Low-alloy steel	UNS N09925 (alloy 925), UNS N07718 (alloy 718), 22Cr or 25Cr duplex SS
Raw seawater	Low-alloy steel with glass-reinforced plastic (GRP) or other liner; unlined low-alloy steel for short design life; titanium (with design limitations)	Titanium (with design limitations)
Produced and aquifer water	Low-alloy steel; low-alloy steel with GRP or other liner; 13Cr (provided oxygen <10 ppb); 22Cr duplex SS, UNS N07718, UNS N09925 (provided oxygen <20 ppb)	13Cr (with limits as for tubing for this service)



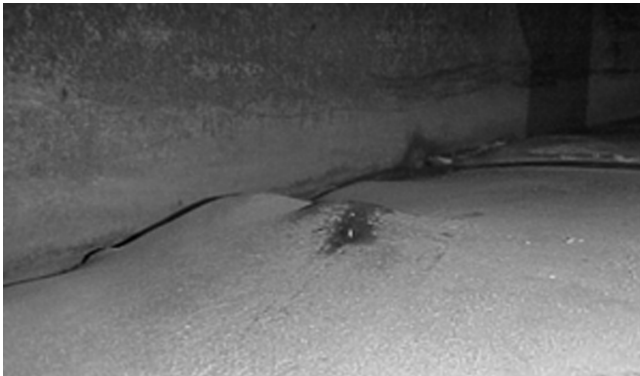
**Figure 8.32** The painted exterior of the same above-ground storage tank shown in Figure 6.18.



**Figure 8.33** Cross section of a typical crude oil AST showing locations where corrosion is likely to occur.

tremendous weight, especially the weight of the exterior walls, which are much heavier than the liquids inside. It is not unusual for tanks to settle unevenly and produce wrinkled bottoms like the one shown in Figure 8.34. These locations can distort and stress the metal so much that cracking and leaking can occur. The uneven bottom also prevents drainage and leads to corrosion. Repeated problems like those shown in Figure 8.34 have led to the development of API inspection standards for ASTs. Figure 8.35 shows the bottom profile of a large fuel-oil AST that was inspected in accordance with API 653. This tank was part of a tank farm less than 20 years old that needed to be replaced due to extensive leaks of hydrocarbon into the local groundwater. Similar tanks, with less settlement at the exterior rings, may last for many decades with only superficial staining of the tank bottoms.

The magnitude of leaks from some of these large storage tanks has led to improved AST design and inspection standards. These are summarized in Table 8.9. Many, if not most, corrosion problems come from



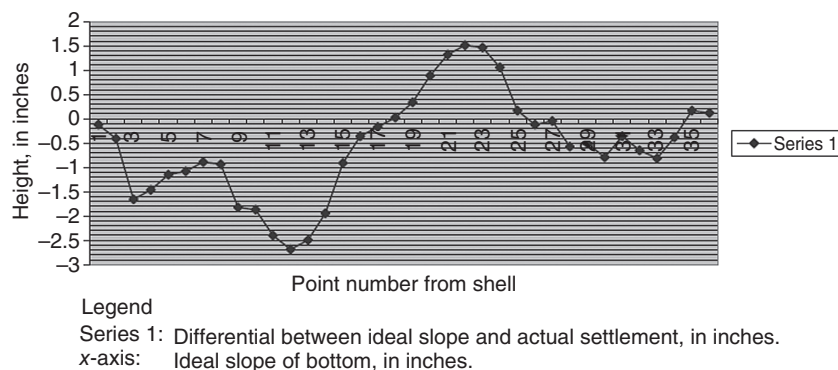
**Figure 8.34** Ring bulging at outer surface of AST tank bottom.

uneven settling of the tremendously heavy walls. Improved guidelines on how to design exterior rings to support these walls has led to major improvements in design, but thousands of existing tanks with internal and external corrosion of the tank bottoms continue in use. Many leaks are not detected until long after they have produced environmental consequences.

The liquid on the interior bottom of a storage tank can be due to produced water, as indicated in Figure 8.33, but it can also be condensation from the vapor

**TABLE 8.9 API Storage Tank Guidelines**

API 510	Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair, and Alteration
API RP 579-1	Fitness-for-Service (Augments the requirements in API 510, API 570, API 653)
API Std 620	Design and Construction of Large, Welded, Low-Pressure Storage Tanks
API Std 625	Selection, Design and Construction of Tank Systems for Refrigerated Liquefied Gas Storage on Land
API Std 650	Welded Steel Tanks for Oil Storage
API RP 651	Cathodic Protection of Above-Ground Storage Tanks
API Std 653	Tank Inspection, Repair, Alteration, and Reconstruction
API Bulletin 939-E	Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service
API Std 2000	Venting Atmospheric and Low-Pressure Storage Tanks: Nonrefrigerated and Refrigerated
API RP 350	Overfill Protection for Storage Tanks in Petroleum Facilities



**Figure 8.35** Inspection profile on the bottom interior of a large fuel-oil AST.

space at the top of the tank that finally settles at the bottom. The drawing in Figure 8.33 is simplified, and a number of vertical supports extend from the vapor space to the bottom of the tank. Water draining along these supports can produce corrosion of the vertical components as shown in Figure 8.36.

The interiors of most ASTs are not coated, and impressed current cathodic protection is frequently used to control corrosion in the water-wetted locations at the bottom of these tanks. Figure 8.37 shows impressed current cathodic protection (ICCP) lead wires from a central power source to openings in the tank roof where vertical anodes are strung to near the bottom of a tank.

Procedures have also been developed to insert liners or to coat AST interior tank bottoms. When repairs are necessary, it is sometime possible to jack up the exterior walls and insert a new bottom flooring over the degraded floor.

Exterior corrosion of tank bottoms can also become a problem, and cathodic protection is frequently used to minimize this corrosion. The use of impermeable membranes or sand layers, which have low electrical conductivity, makes this a difficult proposition in many instances.

### Heat Exchangers

A wide variety of heat exchangers are used in oilfield processing. Shell and tube heat exchangers predominate in the onshore market, but the reduced weight and processing efficiencies of compact heat exchanger designs leads to their extensive use offshore.

**Shell and Tube Heat Exchangers** As stated above, shell and tube heat exchangers are the most commonly



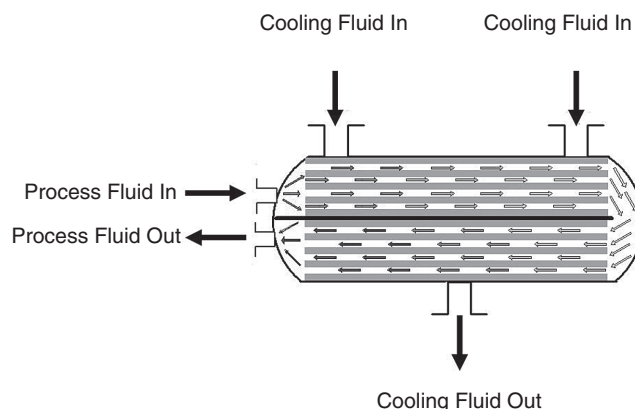
**Figure 8.36** Corrosion on a vertical column at the bottom of a large AST.

used designs for onshore oilfield processing. Figure 8.38 is a simplified view of one of these exchangers. It is common for a tubing bundle to have dozens of tubes as well as intermediate support baffles. Most shell and tube exchangers operate with the process stream on the inside of the tubing and the heat transfer medium (usually cooling water) on the “shell side” between the tubing and the water jacket or water box. After extensive use, it is common for mineral and fouling deposits to form on the outside of the tubing. Thermal expansion and contraction can lead to wear between the tubing and intermediate supports, and this is an area requiring inspection during shutdowns. A variety of nondestructive techniques are available for this purpose.

The tubing in a shell and tube heat exchanger is the thinnest component and is subject to erosion corrosion



**Figure 8.37** Impressed current cathodic protection anode lead wires on the top of a large AST.



**Figure 8.38** Schematic of a small shell and tube heat exchanger.

at the inlets, SCC at locations where the tubing has been expanded into the header plates, fretting and fatigue at intermediate support baffle locations, and so on. Overheating due to scale buildup, fretting corrosion, and erosion corrosion at tubing inlets are the most common forms of tubing failure.

Header plates are frequently made of slightly less corrosion resistant materials. They must be galvanically compatible with the tubing, and it is common practice for copper-nickel or nickel-aluminum bronze headers to be used with both copper-nickel and titanium tubing, although the best practice is to use only one alloy family, for example, copper or titanium for both the tubing, headers, and water box. Crevice corrosion of headers, as shown in Figure 5.28, is a common problem.

Carbon steel water boxes are often used, and it is common for these relatively thick components to have organic protective coatings and galvanic anodes for cathodic protection of the steel. Figure 8.39 shows corroded galvanic anodes in a small onshore heat exchanger.

**Compact Heat Exchangers** Plate frame heat exchangers, brazed aluminum heat exchangers (BAHXs), and printed circuit heat exchangers are all classified as compact heat exchangers. While they are also used onshore, they find their most extensive uses offshore where their weight and size advantages for the same thermal loading lead to significant benefits offsetting their usually somewhat higher capital costs.

Plate frame heat exchangers are the most widely used compact heat exchangers. They are almost universally used for offshore seawater cooling.<sup>36</sup> While there are a number of alloys from which the plates can be manufactured, for this service, commercially pure

titanium (UNS R50400, Grade 2) is the most common, although many organizations specify the palladium-containing grades (UNS R52400 or R52250, Grades 7 or 11 with 0.15 Pd added) for additional elevated temperature crevice corrosion protection. It should be noted that only Grade 2, commercially pure titanium, and Grade 12, UNS R53400, Ti + 0.3 Mo + 0.8 Ni, are approved by NACE MR0175/ISO15156 for H<sub>2</sub>S service, so the use of Grades 7 or 11 is a departure from many companies' practices of only using H<sub>2</sub>S service-approved alloys for any service involving contact with produced fluids.

Recent problems with availability of titanium have led several organizations to try to qualify other CRAs for this service. Ni-Cr-Mo alloys have been recommended for service up to 50°C (122°F) and possibly up to 60°C (140°F).<sup>84,85</sup> It should be noted that these researchers used commercially pure titanium (Grades 1 or 2) as controls, and this is not a direct comparison with the performance of titanium Grades 7 or 11, but the work is an indication that alternatives to titanium may become available, at least at lower seawater temperatures. Figure 8.40 is a schematic of a plate frame heat exchanger showing how it is assembled from many (often 100 or more) deformed thin plates with channels allowing fluid passage. Figure 8.41 shows crevice corrosion at the contact point between two plates. This is the most common form of corrosion on these heat exchangers and is the reason why titanium, with excellent seawater crevice corrosion resistance, has become the standard for this service.

Most failures of these heat exchangers are due to leaking gaskets, which should not be torqued to a specified load; instead they should be tightened to the manufacturer's recommended dimensions.

The principal advantages of these heat exchangers are their relatively light weight. They can also be easily disassembled for cleaning and other maintenance. The disadvantages are relatively limited temperature and pressure ranges dictated by the limitations of the gasket materials.

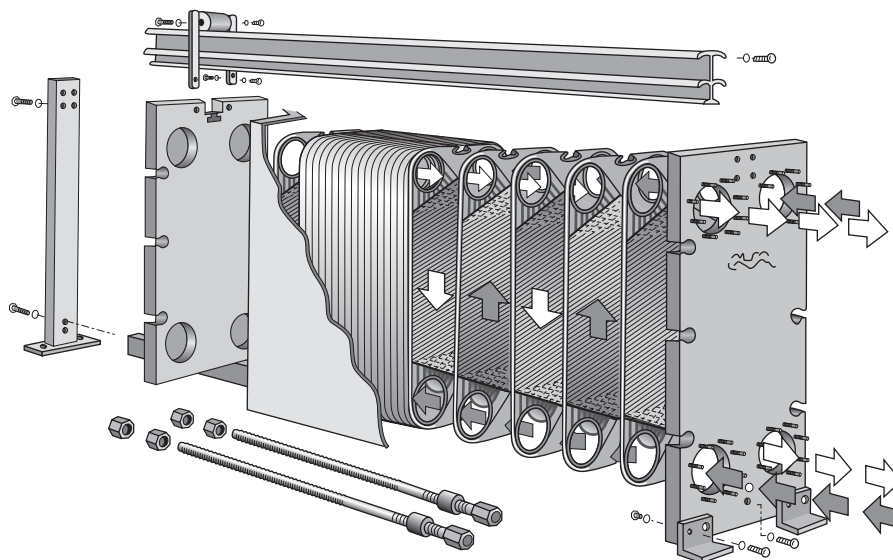
BAHXs (Figure 8.42) find their primary use in natural gas cooling prior to pipeline transport. The units are fabricated from structural sheets with low-melting brazing alloys on the surface and corrugated fluid flow channels. The cross section of one of these heat exchangers looks like a corrugated cardboard box. Once the heat exchanger is assembled, it is heated and the low-melting aluminum brazing alloys flow and form a continuous single-piece cooling unit.

Aluminum is not brittle at cryogenic temperatures and is also very light. BAHXs provide approximately 25 times more surface area for the same weight than conventional shell and tube heat exchangers, and this leads



**Figure 8.39** Magnesium anodes in the water-cooled header space on a gas cooler.





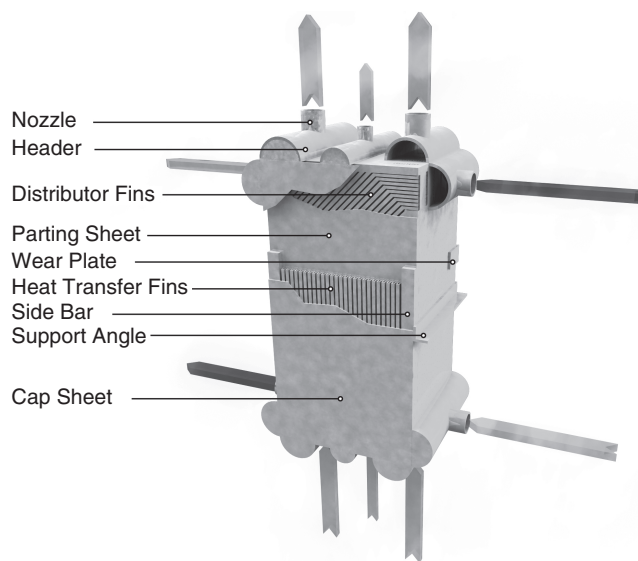
**Figure 8.40** Schematic of a plate-frame heat exchanger. Photo courtesy of Alpha Laval, Inc.



**Figure 8.41** Crevice corrosion at contact point between two plates in a plate-frame heat exchanger.<sup>85</sup>

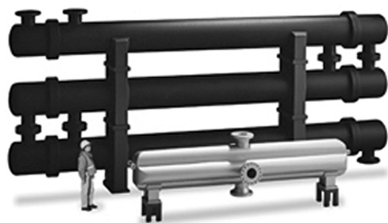
to significant savings in structural support requirements, especially offshore.<sup>36</sup> Limitations of BAHXs are their relatively low operating pressure (approximately 120 bar [1750 psi]), inability to be mechanically cleaned, and their susceptibility to mercury attack. Mercury removal processes are necessary prior to natural gas cooling, and these processes are standard for most offshore natural gas processing designs.

Printed circuit heat exchangers are assembled from plates of electrochemically milled metal that are then assembled in stacks and fusion bonded together. Passages are typically 1–2 mm (0.04–0.08 in.) deep. While they can be fabricated from a number of metals, 316 stainless steel (UNS S31600) is the most common alloy used for these exchangers. These heat exchangers

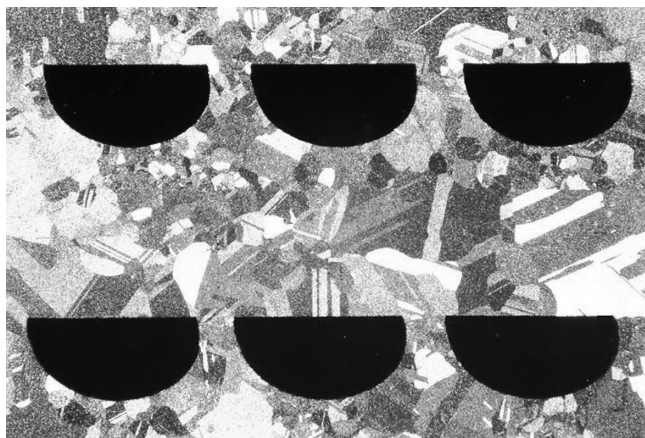


**Figure 8.42** Basic components of a brazed aluminum plate-fin heat exchanger. Drawing courtesy of Chart Heat Exchangers.

are made from stronger materials than BAHXs and can be used at much higher temperatures and at pressures as high as 700 bar (10,000 psi). Unlike aluminum heat exchangers, they are resistant to mercury attack. They have significant weight advantages (approximately 4:1) over shell and tube heat exchangers. Figure 8.43 compares the size of an oilfield printed circuit heat exchanger with the size of three shell and tube heat exchangers having the same thermal and fluid processing capacity.



**Figure 8.43** Comparable printed circuit (foreground) and shell and tube (background) heat exchangers having the same thermal capacity.<sup>86</sup> Figure courtesy of Heatric Division of Meggitt (UK) Ltd.



**Figure 8.44** Cross section of a diffusion-bonded printed circuit heat exchanger.<sup>86</sup> Figure courtesy of Heatric Division of Meggitt (UK) Ltd.

Figure 8.44 is a cross section of a diffusion-bonded printed circuit heat exchanger showing the microstructure of the metal and the fluid passage channels.

Failures of these exchangers over the years are mainly due to thermal cycling and subsequent thermal fatigue. The flow passages have sharp edges that can lead to stress concentrations. If temperatures in the exchanger cycle or fluctuate, the differential expansion and contraction of the core material can lead to fatigue cracking.<sup>36</sup>

Other problems with these heat exchangers include plugging, usually due to upstream debris. They cannot be mechanically cleaned, and plugging or cracking usually means that the heat exchanger must be replaced.

### Other Equipment

Upstream processing of hydrocarbon fluids and associated produced water presents a number of materials challenges. Only a few of the more common problems are addressed in this discussion.

**Steam Injection** Steam is injected into oil-bearing formations to heat the formation and enhance productivity by changing the viscosity of the *in situ* oil.

Most steam injection systems use relatively low-quality steam (meaning that the steam may have appreciable water droplets), but the water must be treated to reduce mineral content or it will result in scaling and plugging of the equipment and the down-hole formations. The methods for water treatment prior to steam injection are similar to those used for power boilers. Feedwater with low solids is selected, or suspended matter is removed by filtration or in settling ponds. Zeolite softeners are then used to remove calcium and magnesium ions that would otherwise form scale in the boilers. Dissolved gases are then removed, usually by mechanical deaeration or by simple heating of the water prior to introducing it into the boiler. Steam deaeration, where hot steam is used to heat the water and drive off dissolved gases, is a common method of removing dissolved gases from boiler feedwater.<sup>87</sup>

Oxygen scavengers lower the dissolved oxygen in the steam and prevent corrosion of the system. The most common oxygen scavengers are sodium sulfite and hydrazine ( $N_2H_4$ ), which is toxic, so the use of hydrazine is discouraged in most localities. pH controls are necessary, and boiler water pH is normally kept near 9. Low pHs promote corrosion, and high pHs can lead to both caustic embrittlement cracking (relatively rare in recent years) and scaling.

**Process Equipment** There is a wide variety of oilfield process equipment. Likely locations where corrosion may occur, as well as recommended inspection procedures and corrosion control techniques, are summarized in Table 8.10.<sup>20</sup>

Process monitoring can indicate when maintenance problems are likely to occur. Figure 8.45 shows sand accumulation due to a “sand event” that produced much more sand than was expected in the free water knock-out vessel on an offshore structure. Table 8.10 warns against corrosion underneath sludge and other deposits on the bottoms of many different vessels.

### Bolting and Fasteners

The terms bolt and fastener are often used interchangeably in oilfield practice. This discussion is related to all threaded fasteners. The term “high strength” is used in the threaded fastener industry to refer to bolts that have been quenched and tempered to develop proper strength. These bolts tend to be low-alloy steels with chrome or chrome-molybdenum additions for thick-section hardenability (Figure 4.27).

**TABLE 8.10 Internal Corrosion and Corrosion Control of Selected Topside Equipment<sup>20</sup>**

System or Equipment (Environment)	Usual Problem Areas	Evaluation Methods (Detection and Monitoring)	Most Common Corrosion Control Methods
Oil Well Produced Fluids Handling Oil and gas separators (traps)	Wet gas area (where water condenses) Free water section (bottom) Water dump valves	Failure history Inspection: visual, sometimes ultrasonic thickness	Coatings Cathodic protection (CP) in the free water Metallurgy of internals and water dump valves
Free water knockout (FWKO)	Free water section, shell, baffles, piping Bottom underdeposits Water dump valves and piping	Failure history Inspection	Coatings Cathodic protection in the free water Periodic flushing and/or bottom cleanout
Heater treaters	Gas section where water condenses Free water and treating sections; shell and baffles, bottom underdeposits Fire tube—particularly under scale deposits Water dump valves and waterlines	Failure history Inspection	Gas section: coatings Fire tube: cathodic protection and/or scale control chemical Free water and treating sections: coating and cathodic protection Routine flushing and cleanout of deposits Siphons and waterlines: coatings and plastics Water dump valves: metallurgy
Gun barrels (wash tanks, settling tanks)	Free water section Under side decks Gas boot and piping in high H <sub>2</sub> S areas Water dump valves	Failure history Inspection	Coatings Cathodic protection in free water Aluminum decks Plastics and nonmetallics for gas boots and piping Water dump valves: metallurgy Oxygen exclusion Routine flushing and cleanout
Lease tanks	Under side of deck Bottom and lower portion of bottom ring	Failure history Inspection	Coatings Aluminum deck Cathodic protection of bottom area if it maintains a water level Oxygen exclusion Routine cleanout of bottom
Hydraulic pumping equipment Power fluid tanks	Power oil tanks—similar to lease tanks		Tanks—coating where appropriate
Power fluid pumps Power fluid lines	Power water tanks— similar to SWD and WI tanks		CP where appropriate Pumps—metallurgy Lines—inhibition All: oxygen exclusion Routine flushing and cleanout Note: Power fluids must be clean

TABLE 8.10 *Continued*

System or Equipment (Environment)	Usual Problem Areas	Evaluation Methods (Detection and Monitoring)	Most Common Corrosion Control Methods
Gas Handling Equipment	Gas-lift systems	Failure history	Dehydration
	Along bottom of line where free water flows or collects		
	On vessel walls where water condenses	Inspection	Oxygen exclusion
			Inhibition on occasion
Coolers	Where water condenses	Failure history Visual inspection, exchanger tube calipers	Metallurgy Neutralization
Accumulators	Where water collects	Failure history Inspection: visual, ultrasonic	Coating Metallurgy
Vessels	Where water collects and in free water portions		Neutralization CP in free water Coatings
		Failure history	
		Inspection: visual, ultrasonic	Neutralization
Compressors	Valves, cylinders, and bottles	Failure history	Metallurgy Inhibition CP in free water
Glycol dehydrator	Wet glycol lines, contactors: trays and shell	Inspection: visual Failure history	Metallurgy
	Regeneration equipment	Inspection Coupons Glycol analysis	pH control Oxygen exclusion Glycol quality
Dry bed dehydrator	Wet gas handling areas, regeneration condensers, etc.	Failure history	Metallurgy
		Inspection	Coatings (where temperature allows)
Water Handling and Injection (Disposal and Flood)			
Vessels and tanks	Shell when water very corrosive	Inspections	Oxygen-free operation (exclusion or removal)
	Bottom underdeposits	Failure history	CP
	Vapor space when sour	Coupons, probes Occasionally iron content and/or bacterial activity	Coatings Periodic cleanout
Filters			Occasionally: biocides or inhibitors
	Connections when bimetallic	Same as vessels	Nonmetals (only for fluids where oxygen exclusion is not important)
	At filter media (sand) level		Same as vessels



**TABLE 8.10** *Continued*

System or Equipment (Environment)	Usual Problem Areas	Evaluation Methods (Detection and Monitoring)	Most Common Corrosion Control Methods
Gathering and injection lines and plant piping	Along bottom underdeposits	Same as vessels	Oxygen-free operation  Coatings and linings (including cement) Periodic line pigging Occasionally: biocides or inhibitors
Injection and transfer pumps	All wetted parts Seals leaking air	Failure history Inspection Galvanic probe (oxygen detector)	Oxygen free operation Metallurgy
Injection wells	Tubing interior, inhole valves, fittings, etc. Wellhead and Christmas tree Annulus above packer (depends on packer fluid)	Failure history  Coupons, probes  Occasionally iron content and/or bacterial activity  Galvanic probes (oxygen detection)	Oxygen-free operation  Coatings and linings (including cement) Occasionally: biocides or inhibitors
Miscellaneous Facilities			
Glycol-water heat transfer systems (heating and cooling)	Anywhere in system (particularly where deposits can occur)	Failure history  Inspection Coupons Fluid analysis Failure history	Inhibition  Oxygen exclusion Fluid quality
Boilers and steam systems	Boiler tubes (including creep and swelling) Condensers and condensate return lines	Inspections  Coupons Iron content Failure history Inspections Coupons Iron content	Water quality control  Deaeration  Inhibition
Gas sweetening (MEA and similar amine systems)	Contact tower Reconcentration system		CO <sub>2</sub> loading Inhibition (usually inorganic) Oxygen exclusion Fluid quality

MEA, methyl ethyl amine.

Bolted connections, flanges, and gaskets are major sources of leaks in oilfield applications. Table 8.11 shows how these problems can account for up to half of all gas leak incidents in a major production area.

Figures 5.6–5.11 showed bolted connections and discussed galvanic corrosion problems associated with bolts. It is important to recognize that bolts are usually the critical component in any assembly, and their corrosion can lead to failure of flanges. Most of the critical areas on a bolted connection are hidden from view, so it is important that appropriate bolts be chosen. While

it is common oilfield practice to blame failures of bolted connections on workers not following established procedures, problems with inappropriate materials and specifications also exist.

Failure modes for bolts include various forms of weight loss corrosion, fatigue, and hydrogen embrittlement, which may be due to environmental exposure or may result from manufacturing processes. Manufacturing processes can strongly affect the resistance of bolts to failure during use. As one example, while most threaded connectors have cut (tapped) threads, rolled threads are



**Figure 8.45** Sand accumulation in a free water knockout tank.

**TABLE 8.11 Norwegian Continental Shelf Gas Leak Incidents<sup>88</sup>**

Year	Total Number Leakage Incidents	Leaks Caused by Mechanical Connections/Gaskets	
		Number of Incidents	Percentage %
1994	194	98	51
1995	117	56	47
1996	171	82	48
1997	177	84	47
1998	248	69	28

**TABLE 8.12 Bolting Materials Used in the Offshore Industry<sup>88</sup>**

Trade Name/Designation	Nominal Composition	Specification/Standard
AISI 4140	Fe-1Cr-0.2Mo	ASTMA193 Grade B7
Alloy A286 Grade	Fe-26Ni-15Cr-2Ti-2Mn-1M	UNSS66286
17-4PH	Fe-16Cr-4Ni-4Cu	UNS S17400/ASTM A693
254 SMO	Fe-20Cr-18Ni-6Mo	UNS S31254
K-500	Ni-30Cu-3Al	UNS N05500
Alloy 725	Ni-21Cr-8Mo-8Fe-3.5Nb	UNS N07725/ASTM B805
Alloy 625, 625 PH	Ni-21Cr-8Mo-5Fe-3.5Nb	UNS N07725/ASTM B805
Alloy 718	Ni-19Cr-17Fe-5Cb-3Mo	ASTM B637
Ti-6Al-4V ELI	Ti-6Al-4	UNS R56400
MP 35N	35Ni-35Co-20Cr-10Mo	UNSR30035

more resistant to fatigue and other forms of cracking than machined threads. The cold working of rolled threads may require stress relief to meet the hardness requirements of NACE MR0175/ISO 15156.

**Materials Used for Oilfield Fasteners** Table 8.12 summarizes a number of the bolting materials used in the offshore oil and gas industry.

Many of these alloys perform their intended function in atmospheric exposure but are not considered appropriate for subsea use because of concerns with hydrogen embrittlement from cathodic protection systems.

The most common structural bolts used in oilfield applications meet the requirements of ASTM A 193 Grade B7. These bolts are made from UNS G 41400 or G414420 (AISI 4140 or 4142) alloy steel with Cr and Mo additions for thick-section hardenability (Figure 4.27). The yield strength of B7 bolts varies from 517 to 723 Mpa (75–125 ksi), depending on the size of the bolt,

which can be up to 178 mm (7 in.) in diameter. Because these bolts receive their strength from the quenching and tempering process, larger bolts have lower yield strengths, although the overall load capacity does increase with diameter. (Figure 4.27).

CRA are also used in the oil field, primarily in applications involving flanges associated with equipment and piping made from similar alloys. The bolts are “matched” to the larger equipment in an attempt to minimize galvanic corrosion effects. An alternative to this approach is the use of dielectric fittings (Figures 5.9 and 5.10), but pressure capabilities of flanges may be lowered due to creep of the washers in these systems. For subsea applications, these dielectric fittings will also isolate bolts and nuts from cathodic protection, and this can lead to stray current corrosion. It is important that any subsea bolted connection be tied into the cathodic protection system.<sup>75</sup>

Stainless and related CRAs that are reported to work for subsea completions include:<sup>75</sup>

- UNS S66286, a precipitation-hardened stainless used for low pressure units
- UNS R30035, a nonmagnetic nickel-cobalt-chromium-molybdenum alloy (MP35N) used at higher pressures
- UNS N09925, a precipitation-hardening nickel-iron-chromium alloy with molybdenum and copper additions
- UNS N07718, a precipitation-hardening nickel chromium iron alloy
- UNS N07725, a precipitation-hardening nickel chromium iron alloy with higher alloying content than UNS N07718. This alloy has better pitting resistance than the others on this list and is probably most suitable for subsea applications.<sup>75</sup>

Several reports indicate that the two precipitation-hardened nickel alloys, UNS N77018 and N07725, are probably the best CRAs for subsea service.<sup>75,89</sup>

Copper-based systems often use aluminum bronze (UNS C63000, ASTM B150) bolts, and most titanium bolts are either UNS R50400, commercially pure titanium, or UNS R56400, titanium with 6% aluminum plus 4% vanadium additions. While CRA alloy bolts are commercially available, they are seldom used because low-alloy heat-treatable steel bolts are much stronger in most cases. Electrical isolation practices like those shown in Figures 5.9–5.11 are available, although some authorities are of the opinion that they are likely to be overcome through inadvertent grounding in many, if not most, instances.

**Embrittlement Concerns** The high-strength nature of most industrial bolts means that they are often made from materials subject to hydrogen embrittlement or environmental cracking. Bolt embrittlement can occur during the manufacturing process, during transportation and storage, or in use. During manufacturing, the alloy steels are quenched and tempered to produce the appropriate strength levels. If this is done improperly, it can lead to brittle bolts.

A more common concern is the effect of corrosion resistant coatings, usually zinc or cadmium, which are applied for atmospheric corrosion control. The pickling process (acid cleaning) prior to coating can result in hydrogen entry into the steel. Electroplating processes also introduce hydrogen. This hydrogen entry is accelerated in most electroplating baths because they usually contain cyanides, which help produce quality electroplates but also act as hydrogen-entry poisons in much the same manner as environmental H<sub>2</sub>S. The standard means of controlling hydrogen embrittlement in electroplated metal is by using a dissolved hydrogen bake-

out procedure at temperatures from 175°C to 205°C (from 350°F to 400°F) for a period of time depending on the size of the part in question.<sup>90–96</sup> Unfortunately, there is no guarantee that all of the hydrogen will be removed from the metal.

Environmental exposure can lead to hydrogen embrittlement of galvanized or electroplated high-strength fasteners at coating holidays, which are inevitable. Hydrogen from atmospheric condensation (typically around pH 5) is enough of a concern that high-strength fasteners are not galvanized because of a concern with hydrogen embrittlement.<sup>97,98</sup>

**NACE RP0176/ISO 15156-2 Guidelines** This standard applies to environmental cracking in the presence of H<sub>2</sub>S. Bolting that will be directly exposed to sour (H<sub>2</sub>S) environments or that will be buried, insulated, equipped with flange protectors, or otherwise denied atmospheric exposure must meet the requirements of this standard, which restricts bolts to the materials shown in Table 8.12 and to a maximum hardness of HRC 22.

The two materials listed are the same, but the ASTM Grade L7M is for use at low temperatures and has fracture toughness testing requirements missing from the more commonly used ASTM A 193 Grade B7M standard.<sup>99,100</sup> The M in the grade designation indicates that the hardness levels for these bolts are held to a maximum of HRC 22, in accordance with the limitations of the NACE/ISO standard. This reduced hardness means that flanges may be derated to lower pressures than would be allowed if standard bolting were used.

**Subsea Embrittlement by Cathodic Protection** At one time, it was thought that limiting subsea bolting to materials that met the requirements of NACE MR0175 would prevent hydrogen embrittlement of fasteners on cathodically protected subsea assemblies. Unfortunately, alloys in the following groups have been found to have hydrogen embrittlement problems when used as fasteners on cathodically protected equipment:<sup>75,101–104</sup>

- Martensitic stainless steels
- Ferritic stainless steels
- Duplex stainless steels
- Nickel-based alloys

It is possible that the reported problems were associated with using metals that were too hard, and studies indicate that hydrogen embrittlement should not be a problem for fasteners if the hardness level is kept at HRC 34 or lower.<sup>75,77,88,89</sup> These hardness levels are much higher than the HRC 22 restrictions for H<sub>2</sub>S service. The discrepancies between reports that hardness levels in

excess of HRC 22 can be used conflict with the requirements of MR0175/ISO 15156 Part 2, which limit hardness levels for any bolts not subjected to atmospheric service to HRC 22.

**Alloys Used for Atmospheric Service** Table 8.13 showed bolting materials that have been used by the offshore industry. While all of these alloys find uses in atmospheric service, several of them have been reported to have hydrogen embrittlement problems when used in subsea applications with cathodic protection. Definitive research on the limitations of most of these alloys is not available.<sup>88</sup>

**Coatings** The great majority of oilfield bolting requirements are met by B7 bolts with protective coatings applied for corrosion control. Generic coatings for fasteners are listed in Table 8.14. Most of these systems do not produce adequate performance for use in offshore and other oilfield applications. The most common coating used for corrosion control is zinc. Most organic coatings are intended for lubricity and quick-disconnect

properties, because many metallic-coated fasteners cannot be unscrewed and must be removed by cutting after several years of atmospheric or immersion service.

Zinc is the most common protective coating for threaded hardware.<sup>106</sup> It can be applied by electroplating, the Sherardizing (mechanical plating) process or, most commonly, by dipping the steel parts to be coated in molten zinc. While the Sherardizing process, which involves vapor deposition of zinc onto steel substrates, is popular in Europe, it is relatively uncommon in other locations. Most precision zinc coatings are thin electroplates, and hot-dipped galvanizing, which produces thicker zinc coatings, typically 1 mil (25  $\mu$ ) or greater, is used more often for corrosion control in aggressive oilfield environments. The atmospheric corrosion protection provided by zinc coatings is roughly proportional to the thickness of the zinc. Thin electroplated coatings may provide protection for 1–2 years, while galvanizing may protect for 10 years or more.<sup>106</sup>

Embrittlement concerns for zinc coatings are addressed by limiting the strength (hardness) levels of zinc-coated metals. Various standards suggest different maximum hardness levels, but HRC 33–35 hardness levels associated with approximately 150 ksi (100 MPa) yield strengths are generally recommended as the dividing line between fasteners subject to environmental hydrogen embrittlement at the inevitable defects in zinc coatings. Common bolting standards and whether they can be galvanized (or zinc electroplated) are shown in Table 8.15. Most of the standards in this table are not applicable to oilfield applications, but ASTM A193

**TABLE 8.13 Carbon and Low-Alloy Steel Acceptable Bolting Materials IAW NACE MR0175/ISO 15156-2<sup>84</sup>**

Bolts	Nuts
ASTM A 193 Grade B7M	ASTM A 194 Grades 2HM, 7M
ASTM A 320 Grade L7M	

**TABLE 8.14 Generic Coating Systems for Threaded Fasteners<sup>105</sup>**

Generic Coating System	DFT, mil ( $\mu$ m)	Maximum Temperature °F (°C)	ASTM B 117 <sup>a</sup> Exposure Hours	Relative <sup>b</sup> Cost Comparison
Uncoated (bare) Steel stud bolt and 2 nuts <sup>b</sup>	N/A	N/A	N/A	1.0
Aluminum plating	0.2–0.3 (5–8)	1000 (540)	1200	1.8
Cadmium plating	0.2–0.3 (5–8)	500 (260)	250	1.6
Ceramic metallic	0.8–1.0 (20–25)	1200 (650)	1000	5.0
Hot-dip galvanizing	1.0–2.5 (25–63)	750 (400)	1500	2.0
Inorganic zinc-rich silicate	1.8–2.4 (45–60)	750 (400)	1500	2.0
Manganese phosphate, fluoropolymer	1.0–1.2 (25–30)	500 (260)	750	3.7
Mechanical zinc	0.2–2.5 (5–63)	750 (400)	400	2.0
Zinc aluminum	0.2–0.50 (5–13)	800 (430)	1000	2.0
Zinc phosphate	0.2–0.50 (5–13)	250 (120)	48	1.5
Zinc phosphate and oil	0.3–0.50 (8–13)	250 (120)	250	1.6
Zinc phosphate, fluoropolymer	1.0–1.2 (25–30)	500 (260)	500	3.7
Zinc plating	0.2–0.3 (5–8)	750 (400)	250	1.6
Zinc plating, fluoropolymer	1.0–1.2 (25–30)	500 (260)	1000	3.7

<sup>a</sup> ASTM B 117 end point is the first sign of red rust.

<sup>b</sup> ASTM A 193 bare steel stud bolt and two nuts, size 0.625  $\times$  4 in. (16  $\times$  100 mm), are used for cost comparisons.

Source: Table 1: Generic Coating Systems for Threaded Fasteners in NACE Report 02107.

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**TABLE 8.15 Recommendations on Galvanizing for Different Bolt Standards**<sup>107</sup>

Grade	Can I Galvanize?	Raw Material	Nominal Size	Minimum Yield Strength	Minimum Tensile Strength	Minimum Hardness
ASTM A325	Yes	Medium Carbon Steel,	1/2"–1"	92	120	C24
ASTM A449	Yes	Quenched and Tempered	1 1/8"–1 1/2"	81	105	C19
SAE J429 Grade 5	Yes		1/4"–1"	92	120	C25
ASTM A193 Grade B7	Yes	Medium Carbon	1 1/8"–1 1/2"	81	105	C19
ASTM A354 Grade BC	Yes	Alloy Steel, Quenched and Tempered	1/4"–2 1/2"	105	125	NA
ASTM F1554 Grade 105	Yes		2 5/8"–4"	95	115	NA
ASTM A320 Grade L7	Yes		1/4"–3"	109	125	C26
ASTM A490	No		2 5/8"–4"	94	115	C22
ASTM A354 Grade BD	No		1/4"–2 1/2"	105	125	NA
SAE J429 Grade 8	No		1/2"–1 1/2"	130	150	C33
			1/4"–2 1/2"	130	150	C33
			2 5/8"–4"	115	140	C31
			1/4"–1 1/2"	130	150	C3

Source: G. Lindsay, *Galvanizing High Strength Bolts*, <http://www.portlandbolt.com/faqs/galvanizing-high-strength-bolts>, April 19, 2010.

Grade B7 is the most common bolting material for oil-field piping. These bolts can be galvanized, and they usually are. Structural bolts are often ASTM A320, which can be galvanized, and ASTM A490, for which the ASTM standard specifically forbids galvanizing.

One of the problems associated with hot-dipped galvanizing is the thickness of the zinc coating, which can make applying nuts difficult. It is common to overlap the nuts used on galvanized bolts to accommodate oversized threads that result from galvanizing. NACE and ASTM provide guidance on this.<sup>105,108</sup>

Cadmium electroplating is sometimes used, but many governments have banned this material due to toxicity questions. It is still acceptable in some locations, and many authorities consider this coating to be superior to electroplated zinc.

It is common to chromate both zinc and cadmium-coated parts to improve the protective qualities of the coating and increase their atmospheric corrosion resistance.

Many oilfield fasteners are covered with fluoropolymer coatings. While they are sometimes marketed for corrosion protection, they are too soft for this purpose and will develop significant holidays during installation. Their proper use is for anti-galling purposes so that the fasteners can be removed with wrenches and perhaps even reused. A variety of fluoropolymers are available for this purpose, and they are marketed using trade names such as Teflon, Viton, Xylan, Hyflon, and Kynar. While the labels imply that they consist of the polymer

implied by the trade name, these coatings, which are usually applied as liquid coatings, all include binder resins that determine most of their corrosion resistance. This means that commercial products having the same fluoropolymer additive may have markedly different corrosion and anti-galling properties.<sup>105,109</sup> Test procedures for evaluating these coating systems are available.<sup>105</sup> Fluoropolymer coating suppliers generally recommend that the metal surface be roughened using phosphate tie coats. The acid phosphating baths can dissolve zinc coatings, and this is another reason why thicker hot-dipped coatings are recommended over much thinner electroplated coatings, which have been known to be entirely removed by phosphating processes.

Makeup torque is lowered by the use of fluoropolymer coatings, and specifications for bolting must be adjusted accordingly.<sup>109</sup>

**Additional Comments on Fasteners** The above discussion has concentrated on bolting materials and coatings. The most corrosive locations in any bolted connection are locations where the bolt shank is shielded from the overall environment in bolt holes. The use of gel lubricants to fill these holes has been successfully reported on offshore structures. Filling the cavity with hydrophobic greases greatly prolongs assembly lives.<sup>109</sup>

Most oilfield piping and similar equipment uses ASTM A193M bolting, because this material is approved by MR0175/ISO 15156-2. Galvanized bolting with fluo-

ropolymer anti-galling coatings are recommended and used by most major operators.

Continued interest in using the best possible CRA bolting materials for subsea materials seems to indicate that precipitation-hardened nickel alloys may find more extensive use in the future. These alloys must be resistant to hydrogen embrittlement caused by cathodic protection systems. At present, the use of these alloys is restricted by the lack of inclusion of any CRAs bolting materials in current versions of NACE MR0176/ISO 15156 which restricts the use of non-listed alloys for bolts not exposed to atmospheric environments. This means that most subsea assemblies, to include pipelines, must use low-alloy bolts.

### Flares

Flares are relatively small components of most processing plants, so materials costs are less important and reliability is emphasized. Many organizations recommend the hottest parts of flares be made from UNS N08800 iron-nickel-chromium alloy, which is recommended for temperatures up to 600°C (1100°F).<sup>110</sup>

Intermediate-temperature alloys having corrosion resistance in the 120–230°C (250–450°F) temperature range include:

- UNS N10276, Hastelloy C-276
- UNS N06200, Hastelloy C-2000
- UNS N06686, Inconel 686
- UNS N06059, VDM Alloy 59
- Acid-resistant bricks

Concerns with atmospheric pollution and energy conservation measures mean that many flares are now being used for intermittent service, and resistance to corrosion at temperatures below the dew point has become important. This means alloys having corrosion resistance below the dew point in the presence of CO<sub>2</sub> and H<sub>2</sub>S. One alloy that may be chosen is UNS N08810, nickel-iron-chromium alloy.

### Corrosion under Insulation

Corrosion underneath insulation (CUI) is a continuing problem in many oilfield processing and steam injection environments. It is common to use stainless steel piping for internal corrosion control, but external corrosion with moisture leaking through metallic jacketing and insulation problems will have either stainless steel or carbon steel piping.

Leaks into insulation systems are inevitable at locations suggested in Figure 3.11 and Figure 8.46. Insulated

equipment should be coated with immersion-grade protective coating systems rated for the service temperature. Tables 8.16 and 8.17 list NACE-recommended coating systems for both austenitic stainless steel and carbon steel equipment.

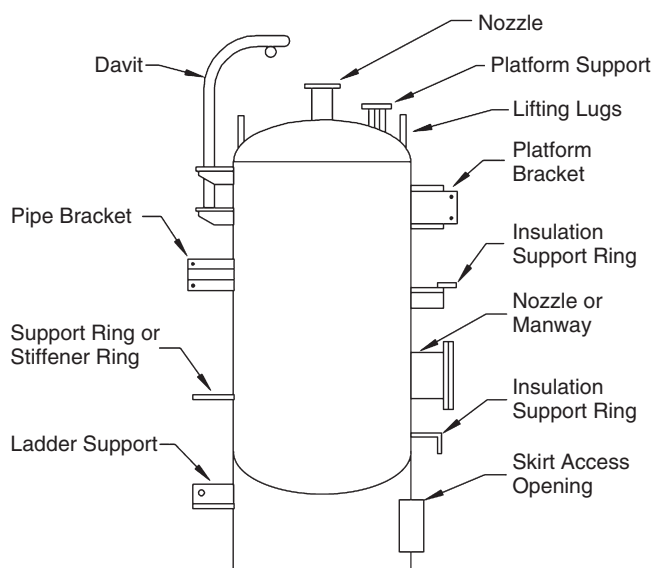
Chilled waterlines are a common problem. Figure 8.47 shows condensation leading to corrosion on a chilled water system where the insulation was not replaced after a repair. The localized nature of CUI is shown in Figure 8.48, where the insulation has been removed and the steel has been sandblasted and repainted prior to placing back in service.

Corrosion control of insulated piping is normally by protective coatings. Tables 8.16 and 8.17 list recommended coating systems to control external corrosion of piping under thermal insulation. Coating systems used for this service should be rated for immersion service at the operating temperatures.

Inspection and detection of CUI is difficult. NACE RP0198 lists several suggestion and approaches.

### PIPELINES AND FLOWLINES

The terms for pipelines and flowlines are somewhat interchangeable. Many organizations consider flowlines to be piping systems, sometimes buried and sometimes on the surface, that carry fluids from wells to processing equipment. Once fluids are separated or treated in some manner, the term pipeline becomes the generally accepted term, and these pipelines will often extend for many kilometers (miles). Figure 8.49 shows causes of



**Figure 8.46** Typical vessel attachments where water may bypass insulation.<sup>111</sup>

**TABLE 8.16 Protective Coating Systems for Austenitic Stainless Steels under Thermal Insulation<sup>112</sup>**

Substrate	Temperature Range <sup>a</sup>	Surface Preparation	Surface Profile <sup>b</sup>	Prime Coat <sup>c</sup>	Finish Coat <sup>c</sup>
Austenitic Stainless Steel System No. 1	−45 to 60°C (−50 to 140°F)	NACE No. 3/ SSPC <sup>d</sup> -SP 6 <sup>e</sup>	25 to 50µm (1 to 2 mil)	130µm (5 mil) of high-build (HB) epoxy	N/A
Austenitic Stainless Steel System No. 2	−45 to 150°C (−50 to 300°F)	NACE No. 3/ SSPC-SP 6	25 to 50µm (1 to 2 mil)	150µm (6 mil) of epoxy/phenolic or high-temperature-rated amine-cured coal tar epoxy	150µm (6 mil) of epoxy/phenolic or high-temperature-rated amine-cured coal tar epoxy
Austenitic Stainless Steel System No. 3	−45 to 370°C (−50 to 700°F)	NACE No. 3/ SSPC-SP 6	25 to 50µm (1 to 2 mil)	50µm (2 mil) of air-dried modified silicone coating	50µm (2 mil) of air-dried modified silicone coating
Austenitic Stainless Steel System No. 4 <sup>f</sup>	−45 to 760°C (−50 to 1400°F)	NACE No. 3/ SSPC-SP 6	40 to 65µm (1.5 to 2.5 mil)	100µm (4 mil) siloxane	100µm (4 mil) siloxane

<sup>a</sup> The temperature range shown for a coating system is that over which the system is designed to maintain its integrity and capability to perform as specified when correctly applied. However, the user may determine whether any coating system is required, based on corrosion characteristics of stainless steel at certain temperatures.

<sup>b</sup> A typical minimum and maximum surface profile is specified for each substrate. Acceptable profile range may vary, depending on substrate and type of coating. Coating manufacturer's recommendations should be followed.

<sup>c</sup> Coating thicknesses are typical dry-film values. Temperature ranges are typical for the coating system. For protective coatings not listed, specifications and coating manufacturer's recommendations should be followed.

<sup>d</sup> SSPC: The Society for Protective Coatings (SSPC), 40 24th Street 6th Floor, Pittsburgh, PA 15222-4656.

<sup>e</sup> NACE No. 3/SSPC-SP 6 (latest revision), "Commercial Blast Cleaning" (Houston, TX: NACE, and Pittsburgh, PA: SSPC).

<sup>f</sup> This system is not recommended for cyclic service characterized by rapid temperature fluctuations.

**TABLE 8.17 Protective Coating Systems for Carbon Steels under Thermal Insulation and Cementitious Fireproofing<sup>112</sup>**

System Number	Temperature Range <sup>a,b</sup>	Surface Preparation	Surface Profile, µm (mil) <sup>c</sup>	Prime Coat, µm (mil) <sup>d</sup>	Finish Coat, µm (mil) <sup>d</sup>
Carbon Steel System No. 1	−45 to 60°C (−50 to 140°F)	NACE No. 2/ SSPC-SP 10	50–75 (2–3)	High-build epoxy, 130 (5)	Epoxy, 130 (5)
No. 2 (shop application only)	−45 to 60°C (−50 to 140°F)	NACE No. 2/ SSPC-SP 10	50–75 (2–3)	N/A	Fusion-bonded epoxy (FBE), 300 (12)
No. 3	−45 to 150°C (−50 to 300°F)	NACE No. 2/ SSPC-SP 10	50–75 (2–3)	Epoxy phenolic, 100–150 (4–6)	Epoxy phenolic, 100–150 (4–6)
No. 4	−45 to 205°C (−50 to 400°F)	NACE No. 2/ SSPC-SP 10	50–75 (2–3)	Epoxy novolac or silicone hybrid, 100–200 (4–8)	Epoxy novolac or silicone hybrid, 100–200 (4–8)
No. 5	−45 to 595°C (−50 to 1,100°F)	NACE No. 2/ SSPC-SP 5	50–100 (2–4)	TSA, 250–375 (10–15) with minimum of 99% aluminum	Optional: Sealer with either a thinned epoxy-based or silicone coating (depending on maximum service temperature) at approximately 40 (1.5) thickness
No. 6	−45 to 650°C (−50 to 1,200°F)	NACE No. 2/ SSPC-SP 10	40–65 (1.5–2.5)	Inorganic copolymer or coatings with an inert multipolymeric matrix, 100–150 (4–6)	Inorganic copolymer or coatings with an inert multipolymeric matrix, 100–150 (4–6)
No. 7	60°C (140°F) maximum	SSPC-SP 2 or SSPC-SP 3	N/A	Thin film of petrolatum or petroleum wax primer	Petrolatum or petroleum wax tape, 1–2 (40–80)

**TABLE 8.17** *Continued*

System Number	Temperature Range <sup>a,b</sup>	Surface Preparation	Surface Profile, $\mu\text{m}$ (mil) <sup>c</sup>	Prime Coat, $\mu\text{m}$ (mil) <sup>d</sup>	Finish Coat, $\mu\text{m}$ (mil) <sup>d</sup>
No. 8 Bulk or shop-primed pipe, coated with inorganic zinc	-45 to 400°C (-50 to 750°F)	Low-pressure water cleaning to 3,000 psi (20 MPa) if necessary	N/A	N/A	Epoxy novolac, epoxy phenolic, silicone, modified silicone, inorganic copolymer, or a coating with an inert multipolymeric matrix, is typically applied in the field. Consult coating manufacturer for thickness and service temperature limits <sup>e</sup>
No. 9 Carbon steel under fireproofing	Ambient	NACE No. 2/SSPC-SP 10	50–75 (2–3)	Epoxy or epoxy phenolic, 100–150 (4–6)	Epoxy or epoxy phenolic, 100–150 (4–6)
No. 10 Galvanized steel under fireproofing	Ambient	Galvanizing: sweep blast with fine, nonmetallic grit	25 (1)	Epoxy or epoxy phenolic, 100–150 (4–6)	Epoxy or epoxy phenolic, 100–150 (4–6)

<sup>a</sup> The temperature range shown for a coating system (including thermal-cycling within this range) is that over which the coating system is designed to maintain its integrity and capability to perform as specified when correctly applied. However, the owner may determine whether any coating system is required, based on corrosion resistance of carbon steel at certain temperatures. Temperature ranges are typical for the coating system; however, not all coatings in a category are rated for the given minimum/maximum temperature. Specifications and coating manufacturer's recommendations should be followed for a particular coating system.

<sup>b</sup> Temperature range refers to the allowable temperature capabilities of the coating system, not service temperatures.

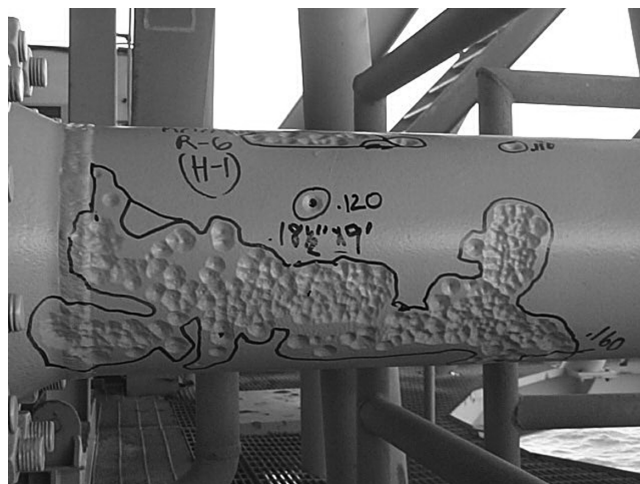
<sup>c</sup> Typical minimum and maximum surface profile is given for each substrate. Acceptable surface profile range may vary, depending on substrate and type of coating. The coating manufacturer's recommendations should be followed.

<sup>d</sup> Coating thicknesses are typical DFT values, but the user should always check the manufacturer's product data sheet for recommended coating thicknesses.

<sup>e</sup> If inorganic zinc-rich coating is applied in a shop and topcoat is applied in the field, proper cleaning of the inorganic zinc-rich coating is required. The use of inorganic zinc-rich coating under insulation is not a preferred system for service temperatures in the CUI range up to approximately 175°C (350°F). However, bulk piping is often coated with inorganic zinc-rich coating in the shop and some owners purchase this piping for use under insulation. In these cases, the inorganic zinc-rich coating should be topcoated to extend its life.



**Figure 8.47** Condensation on the surface of an insulated chilled waterline where the insulation has not been replaced after repairs.



**Figure 8.48** Pitting corrosion underneath insulation on an offshore piping system.

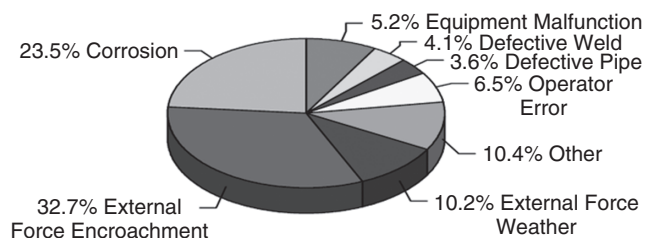


onshore gas pipeline failures.<sup>112</sup> The numbers change, but the trends are roughly similar for liquid petroleum pipelines. Corrosion is the second most common form of pipeline failures, exceeded only by external forces, often termed third-party damage, which is often construction activity related (Figure 8.49).

The percentage numbers differ, but the trends are the same for liquid petroleum pipelines. For offshore pipelines, one half of all reportable incidents are due to corrosion, with 69% due to external corrosion and 31% reported to be caused by internal corrosion.<sup>113</sup>

Figure 1.2 showed some of the consequences of a fatal pipeline explosion near Carlsbad, New Mexico in 2000. Up until that time, most corrosion efforts on “sales gas” pipelines were concentrated on external corrosion. One of the lessons learned from this incident is that internal corrosion is also important and deserves attention.

Figures 8.50 and 8.51 show the forces associated with gas pipeline ruptures. Fortunately, the corrosion pitting of a wrapped spiral-welded pipeline with external corrosion happened in a remote location and no injuries resulted. The energy stored in compressed gases of all



**Figure 8.49** Causes of gas pipeline failures.<sup>112</sup>



**Figure 8.50** Crater caused by a natural gas pipeline explosion.

types makes gas pipelines more dangerous than oil pipelines, even though both transport flammable liquids.

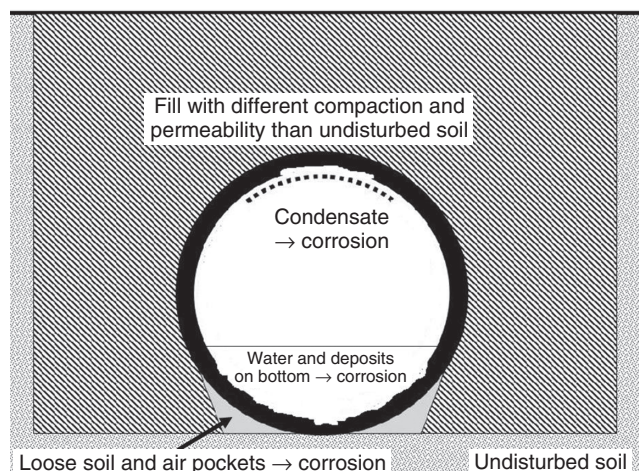
The 2006 Prudhoe Bay crude oil leaks received worldwide attention.<sup>114–117</sup> The spills caused environmental and economic damages that were still being debated years after the incidents. One of the unforeseen consequences of these incidents is that the corrosion control and maintenance budgets of many oil companies were increased as a result of improved management awareness of the consequences of corrosion of pipelines and other equipment.

### Pipeline Problems and Failures

Pipeline corrosion can be either external or internal. Locations where corrosion is most likely are shown in Figure 8.52. Internal corrosion will occur at the bottom,



**Figure 8.51** Part of the pipeline shown in Figure 8.50.

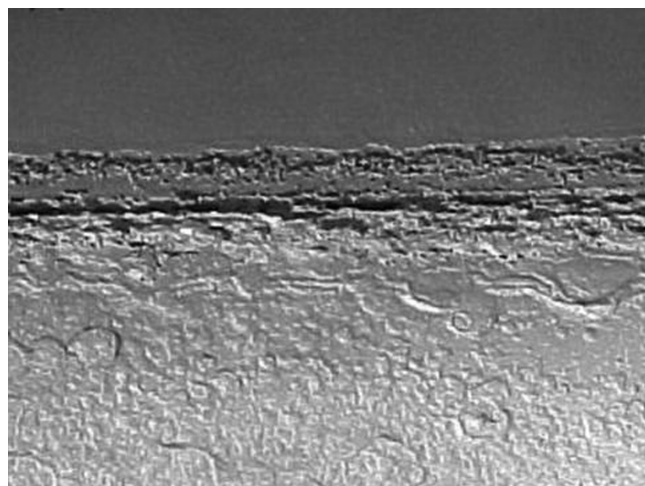


**Figure 8.52** Radial locations where corrosion is most likely on buried pipelines.

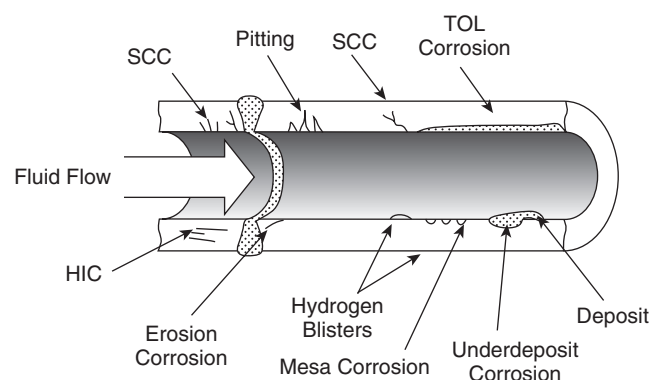
or 6 o'clock position, where water and debris are likely to accumulate, and near the top of multiphase systems, where condensation creates corrosive conditions in the absence of corrosion inhibitors. External corrosion of buried pipelines is most likely near the 4 and 8 o'clock positions, where the lack of soil compaction is likely to leave air voids that can become wetted with groundwater.

Figure 8.53 is a photograph showing the uncorroded top interior of a natural gas pipeline and the pitting corrosion associated with water and biofilm collection near the bottom. Note how the liquid phase levels have changed, leading to various depths of pitting attack at the liquid-gas interface.

Construction activities and repairs will also create galvanic cells between the disturbed soil near new pipe and adjacent older pipe that has been buried for longer times (Figure 5.17).



**Figure 8.53** The interior of a natural gas pipeline showing the lack of corrosion in the gas phase and extensive pitting corrosion in the water and condensate phase.



**Figure 8.54** Forms of corrosion found on pipelines.

Fatigue failures occur when suspended pipelines encounter vortex shedding due to subsea or river currents.<sup>118</sup>

### Forms of Corrosion Important in Pipelines and Flowlines

Table 8.18 and Figure 8.54 list the forms of corrosion associated with the worldwide operating conditions of a major oil company's pipelines. The list in Table 8.18 does not consider corrosion mechanisms not controlled by operations, for example, those forms of degradation addressed by proper design and construction practices. These include the various forms of environmental cracking controlled by appropriate materials selection and welding procedures and, in general, not influenced by operating conditions,<sup>119</sup> although some forms of SCC might also be characterized as corrosion fatigue, because they are accelerated by differences in operating pressures in gas pipelines.<sup>120</sup>

Many of the pictures in Chapter 5, Forms of Corrosion, show corrosion on pipelines. The most serious corrosion problems come from pitting corrosion and from environmental cracking. Both forms of corrosion can be due to either internal or external environments and can lead to unexpected pipeline failures. It is not uncommon for corrosion pits to serve as stress risers leading to SCC failures.

Microbially influenced corrosion (MIC) is also a serious concern and has been associated with both the Carlsbad gas pipeline failure and the Prudhoe Bay crude oil pipeline leaks.

**TABLE 8.18** Corrosion Mechanisms Associated with Pipeline Maintenance<sup>119</sup>

	Corrosion Mechanism
Internal corrosion	CO <sub>2</sub> /H <sub>2</sub> S weight loss corrosion including preferential weld corrosion and corrosion under deposits Top-of-line corrosion (TLC) Microbially induced corrosion (MIC) Erosion corrosion Erosion by solids Galvanic corrosion and corrosion at insulating joints (external CP) Corrosion by oxygen
External corrosion	Atmospheric corrosion Corrosion in splash and transition zones, including river crossings Corrosion in buried/immersed conditions Erosion and erosion corrosion including external (shore landing and river crossing) Stray currents and interferences



A form of corrosion unique to gas and multiphase pipelines is top-of-the-line corrosion. At locations where temperatures and pressures allow condensation, the condensate is frequently a mixture of low-mineral content water and hydrocarbons, including acetic and formic acid. (Figure 8.55). This condensate is corrosive and causes internal corrosion near the top (12 o'clock position) on many pipelines. Corrosion inhibitors are often concentrated in water at the bottom of these same pipelines. Inhibitor pigs, including newly developed spray pigs, have been developed to recycle film-forming corrosion inhibitors from the bottom to the top of pipelines in attempts to control this form of corrosion.

Black powder (Figure 8.56), deposits found in pipelines including iron sulfides and oxides, hydrocarbon solids, and other debris, is a major problem associated with pipelines. This powder can accumulate in low-

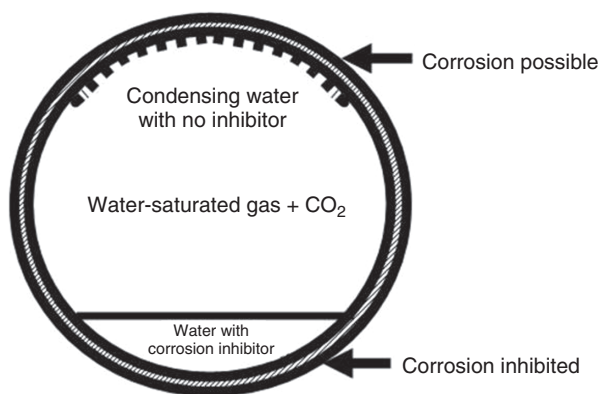
velocity locations in pipelines and has been known to block flow. It can also cause underdeposit (crevice) corrosion.<sup>120, 121</sup>

### Repairs and Derating Due to Corrosion

Several guidelines require various corrosion allowances for pipelines, but most pipeline corrosion is localized and can lead to relatively deep penetration or cracking with little average wall loss. Figure 8.57 shows a grid pattern marked on a pipeline exterior. The purpose of mapping these corrosion pits is to determine if clustered pits are close enough to act as a somewhat larger defect or if the individual pits act independently. Similar calculations, based on defect depth and proximity to other defects, are used to calculate if environmental cracking defects are too close and act as larger defects.

Software programs overestimate the remaining strength and are not conservative enough in some cases when applied to older pipelines, which are considered to be brittle compared to steels produced since approximately 1990. While various software programs have been shown to work quite well based on laboratory and field tests on modern pipeline steels,<sup>122-127</sup> they may overestimate the safe operating pressures for steel manufactured by earlier production methods.<sup>128</sup> Pipeline steels were not controlled for brittle properties prior to changes in API 5L requirements introduced in the year 2000 revision of the standard. Steels manufactured before that date may be brittle, and have not been tested for ductile-brittle behavior.

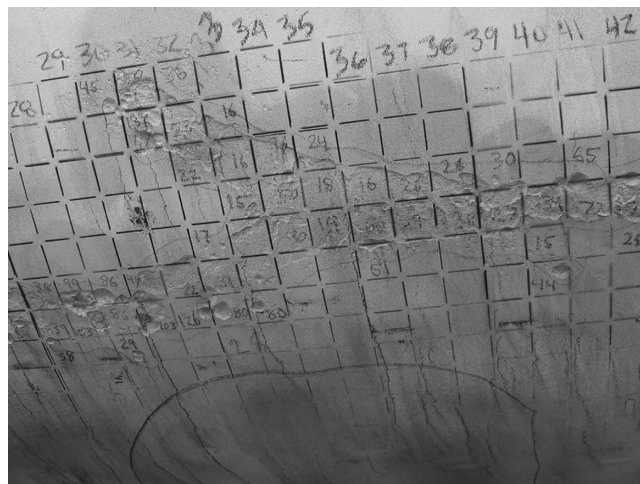
Pipeline repair methods often employ installation of sleeves over corroded areas (Figures 8.58 and 8.59).<sup>129</sup> The strength of these sleeves depends on the quality of



**Figure 8.55** Condensation leading to top-of-the-line corrosion in gas and multiphase pipelines.



**Figure 8.56** Black powder removed from a gas pipeline at a pig trap.



**Figure 8.57** Grid pattern marked on the exterior of a pipeline.



**Figure 8.58** Installation of a pipeline repair sleeve over a corroded pipeline leak.

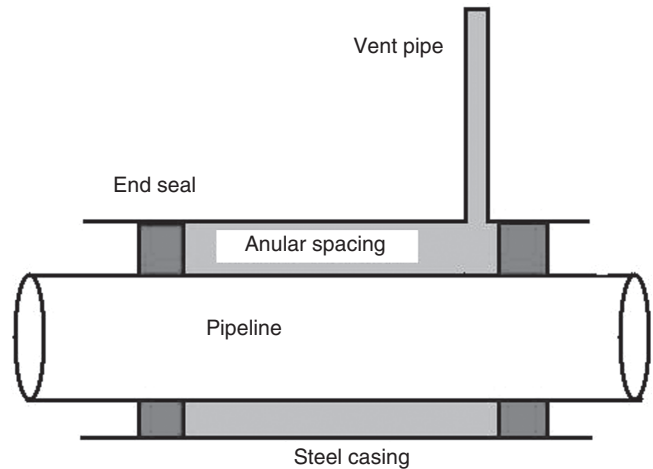


**Figure 8.59** Repair sleeves installed on corroded crude oil pipeline.

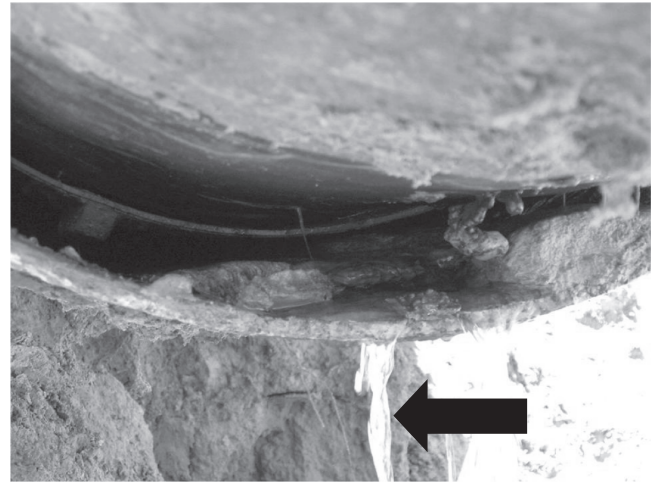
installation, and manufacturer's recommendations concerning safe operating levels often overestimate safe operating pressures. This is especially true with composite sleeves, which have become popular in recent years, because they do not require welding and can often be applied without depressurization of operating pipelines.<sup>130</sup>

### Casings for Road and Railway Crossings

Figure 8.60 shows the idea of pipeline casings for road and railway crossings. A strong outer pipe (casing) surrounds the inner carrier pipeline that contains the fluids being transported in the pipeline. Electrical insulators are installed to isolate the two pipes, seals are intended to keep moisture from the annular spacing between the two pipes, and vents are installed so that any moisture or leaking fluid can escape from the casing annulus.<sup>131</sup>



**Figure 8.60** Pipeline casing for road or railway crossing.



**Figure 8.61** Water leaking from a defective pipeline casing annular space. Arrow indicates dripping water.

Perceived benefits from the use of casings include the following:

- Casings provide structural support and protect carrier pipes from vibrations and surface motion ("live loads").
- Casings protect carrier pipes from the dead weight of the structures above them.
- Vents allow the escape of dangerous material from the right of way.
- Casing systems make leak detection easier.

Problems associated with pipeline casings include:

- Seals between casings and carrier pipes can leak and fill the casing with corrosive water. This is shown in Figure 8.61.



- They can also become electrically shorted, invalidating cathodic protection on the carrier pipe.

There are many problems associated with installation and maintenance of pipeline casings, and most authorities recommend against their use, except where required by regulatory agencies. Deeper burial of conductor pipes or the use of thicker steel at crossings are recommended to avoid the need for casings except where required by regulatory agencies, railroad operators, and so on. Developments in onshore directional drilling have enabled many pipelines to be installed at greater depths, eliminating requirements for pipeline casings.

### Pipeline Materials

Most pipelines are constructed from carbon steel in accordance with API 5L or similar standards, although there has been a tendency for subsea pipelines to be constructed from martensitic stainless steels (13Cr) in recent years because of concerns with internal corrosion.

The installed costs of subsea pipelines and flowlines are divided approximately equally between materials (assuming carbon steel), lay barge and welding, seabed preparation, and insulation and weight coating. Thus, doubling the cost of materials by changing from carbon steel to martensitic stainless steel (13Cr) is sometimes considered justified. The doubling of the costs for materials and welding only increases the total costs by about 25%. Compared to the costs of lost production and repairs, this is often considered to be a justified expenditure.

All stainless steels have problems with crevice corrosion, so subsea or buried stainless steels must have the same external corrosion control measures—coatings supplemented by cathodic protection—that are used for carbon steel pipelines. Unfortunately, welding problems have been reported for in-service stainless steel pipelines.<sup>132–134</sup>

Martensitic stainless steels offer increased corrosion resistance to CO<sub>2</sub> corrosion but only limited resistance for mild H<sub>2</sub>S service. For high H<sub>2</sub>S applications, it is necessary to use much more expensive CRAs. This is why sour gas is usually processed relatively close to the source whereas CO<sub>2</sub>-rich fluids are sometimes transported for long distances in 13Cr multiphase pipelines before onshore or centralized processing.

Untempered martensite (called “hard spots” in pipeline terminology) can occur due to improper thermomechanical processing in pipe fabrication mills or due to improper welding procedures. Magnetic flux leakage (MFL) inspections can identify hard spots. This untem-

pered martensite can occur in carbon steels, 13Cr pipeline steels, and selected other ferrous metals.

Hard spots can be detected by MFL inspection.<sup>135</sup> Unfortunately, it is often necessary to do this after field failures have indicated that entire shipments of questionably processed pipe have been delivered, installed, and placed in service.

The most common grade of API line pipe is X65 with specified minimum yield stresses of 65 ksi. Grades as high as X80 have been accepted and used with minimal concerns about environmental hydrogen embrittlement, which can come from internal fluids; from H<sub>2</sub>S-rich soils, for example, due to anaerobic bacteria; or from cathodic protection. Steel producers are developing higher-strength pipelines, and the claimed advantages are reduced material shipping costs and lower weights in transport.<sup>136</sup> For most construction, the weight of pipes is a secondary concern, and offshore and other submerged pipelines frequently require concrete weight coatings (Figure 8.62) to provide negative buoyancy.

The steels used in pipelines have changed over the years, even though most pipelines are still constructed from carbon steels. In the 1970s, hot rolling followed by normalizing was replaced by thermomechanical processing. Continuous casting processing has resulted in an unfortunate tendency for the “cleaner” steels produced in recent years to have more segregation and inclusions near the middle of plate steels. Varying minor alloying additions produce higher-strength fine-grained steels with improved weldability.<sup>137,138</sup> The results of these improvements are generally better steels, and the introduction of ductility testing requirements to API 5L in 2000 means that newer pipelines are less likely to



**Figure 8.62** Concrete weight coating on the exterior of pipe intended for submerged service.

have some of the brittleness problems (hydrogen embrittlement in its various forms plus low ductile-brittle transition temperatures) associated with older pipelines. Unfortunately, much of the existing pipeline infrastructure was built before these improvements were introduced.

A major problem associated with pipeline steels in the past has been welding. Spiral-welded pipe, used extensively in Canada and Europe, is still considered a lower-grade of pipe in many other locations, although major pipelines in the United States were constructed using spiral-welded piping in recent years due to non-availability of conventional longitudinally welded pipe. Seamless pipe is only available in relatively small diameters (up to approximately 16 in. or 410mm). Welding still remains the most likely location for metallurgical defects on pipelines. The practice of orienting joints of pipe so that the longitudinal welds are at 2 o'clock on one joint and 10 o'clock on the next joint (Figure 4.24) is intended to prevent any cracks that do form from running from one joint to the next joint. The 2 o'clock and 10 o'clock positions are chosen to avoid the most likely orientations for internal corrosion (6 o'clock and 12 o'clock) or external corrosion (4 o'clock and 8 o'clock) (Figure 8.52).

### Hydrotesting

Hydrotesting is a common means of testing the integrity of pipelines after construction, major alterations, or repairs. The procedure involves filling the pipeline (or other pressure vessels) with water and pressurizing the system to a level higher than the anticipated maximum allowable operating pressure (MAOP), usually 125% of MAOP. This test is intended to identify any defects, either corrosion or, more likely, sharp defects associated with welding or environmental cracking. Hydrotesting may increase resistance to environmental cracking by slowing the growth rates of preexisting cracks, but the primary purpose is to locate and repair defects before

the equipment is placed or returned to service.<sup>121,139,140</sup> Water used for hydrotesting should be as clean as possible (Table 8.19). While clean water sources are often used for smaller equipment, the large volumes of water needed to pressurize pipelines means that river, lake, or ocean water is usually used.

The main problem associated with hydrotest water is MIC. Biofilms will form on metal surfaces within 48h–2 weeks, and can cause significant corrosion within a month. Mature biofilms are resistant to biocides, so biocide treatments should accompany initial flooding of the equipment, unless the equipment can be drained within 3–5 days of testing.<sup>140</sup> Table 8.20 shows typical concentrations of bacteria in natural waters, and Table 8.21 lists the generic types of biocides commonly used in pipeline hydrotest waters.<sup>140</sup>

Dissolved oxygen will normally be consumed in the first days of the test and will not produce appreciable corrosion unless air pockets form. Oxygen scavengers are not recommended, because they will often interfere with biocides, which are usually necessary.<sup>140</sup>

Many pipelines cannot be drained efficiently, and biofilm removal using scraper pigs is often advised before placing pipelines in service. MIC problems can be significant for pipelines operating in the 15–45°C (60–115°F) range. At temperatures above 80°C (180°F), the risks are minimal.<sup>140</sup>

### External Corrosion

External corrosion control of pipelines is considered a well-developed technology, although questions and controversies associated with industrial practices still arise. The use of organic coatings to protect metallic pipelines dates to 1830 in England. Cathodic protection of pipelines was reported around 1906 in Germany and was popularized by Kuhn and coworkers in Louisiana. Kuhn suggested the use of a protection potential of –850 mV Cu/CuSO<sub>4</sub> in 1933, and led efforts to found NACE in the 1940s.<sup>141</sup>

**TABLE 8.19 Water Sources Used for Hydrotesting Pipelines and Other Pressurized Equipment<sup>140</sup>**

Water Source	
Demineralized water	Most desirable
High-purity steam condensate	
Potable water	
Seawater (clean, more than 50ft above seabed and 50ft below sea surface)	↑
River water	
Lake water	
Brackish water	Least desirable

**TABLE 8.20 Typical Concentrations of Bacteria in Natural Waters<sup>140</sup>**

Location	Concentration (cells/mL)
Seawater	
Continental shelf and upper 200m of open ocean	$5 \times 10^5$
Deep water (below 200m)	$5 \times 10^4$
Deep water (below 320m)	$10^2$
Freshwaters and saline lakes	$10^6$
Potable water	$10^5$

**TABLE 8.21 Properties of Biocides Used for Pipeline Hydrotesting<sup>140</sup>**

Property		Biocide		
		Quaternary Amine	Glutar-Aldehyde <sup>27,32</sup>	THPS <sup>33</sup>
pH stability range		5–9	5–9	2.5–9
Oxygen stability		Excellent	Poor	Poor
Half-life (days)	Biotic anaerobic	100s of days	River water and sediment: <1 Seawater: 32.5	Seawater: 72 days at pH 7 7 days at pH 9
	Biotic aerobic	100s of days	Seawater: <1	Seawater: <1 day to THPO 25 days to complete degradation
Wetting ability		Good	Improved with surfactant addition	Requires surfactant addition
Treatment of hydrotest water required at end of use?		Yes	Yes	Yes (may not need treatment dependent on discharge water test results)

THPS, tetrakis(hydroxymethyl) phosphonium sulfate; THPO, tris(hydroxymethyl)phosphine oxide.

The standard way of protecting pipelines from external corrosion is to use protective coatings as the primary means of corrosion control, with cathodic protection systems as the secondary, or supplementary corrosion control technique. Cathodic protection systems are sized and designed to provide sufficient electrical current to protect exposed metal at holidays in new coatings and to provide more electrical current as protective coating systems age and become less effective. While cathodic protection can be applied to uncoated pipelines, reductions in electric current due to protective coatings have been shown to be the preferable approach to external pipeline corrosion control. In current practice, virtually all hydrocarbon pipelines have a combination of protective coatings supplemented by cathodic protection. Gathering lines, which may have shorter intended service lives, are sometimes protected only by protective coatings.

Chapter 6, Corrosion Control, has extensive discussions of protective coatings and cathodic protection. While protective coatings have many uses and applications, most of the discussions of cathodic protection in Chapter 6, and in the worldwide cathodic protection literature, relate to pipelines and associated equipment.

One of the problems with cathodically protected pipelines is hydrogen embrittlement. This is normally handled by only using pipeline steels that are resistant to hydrogen embrittlement, and this is one reason why most pipelines are limited to steels having yield strengths of 80 ksi (550 MPa). This practice seems to work in most cases, although there is some question about hydrogen charging in concentrated brines in permafrost soils.<sup>138</sup>

Protective coating systems for pipelines have changed over the years as new coating systems have been developed and problems with existing systems have been identified. Current buried and submerged pipeline protective coating practices include the following coatings systems:

- Fusion-bonded epoxy (most widely used on pipelines)
- Multilayer polyethylene systems—often with epoxy primer and copolymer adhesive layers below the polyethylene surface coating (most widely used on pipelines).
- Extruded thermoplastic systems—commonly used on small-diameter pipelines and other piping systems (most widely used on pipelines)
- Multilayer polyurethane—similar to polyethylene and less common
- Asphalt/coal tar enamels—health and safety issues limit their use in many locations, and they are sometimes banned from use. Their market share is declining worldwide.

Pipeline tapes and wraps were common at one time, but their market share has been reduced in recent decades due to problems including disbonding and dielectric shielding of cathodic protection. Their use on pipelines is largely restricted to complicated shapes and to repair and rehabilitation projects.

Disbonded coatings have been found to shield cathodic protection currents and lead to external pipeline corrosion. This is shown in Figure 8.63. Proper





**Figure 8.63** Debonded pipeline coating.



**Figure 8.64** Blisters on fusion-bonded epoxy-coated gas transmission pipeline. Note the pH 12 water stains dripping from the broken blister. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

surface preparation is necessary to insure that coatings adhere to the steel substrate. Disbonding can also be caused by cathodic protection, and ASTM standards have been developed to test coating systems for resistance to coating disbonding at coating holidays.<sup>142,143</sup>

One of the claimed advantages of fusion-bonded pipeline coatings is that if they are damaged and holidays are formed, the holidays do not shield cathodic protection currents from reaching the surface. This is shown in Figures 8.64 and 8.65, which show the exterior of a gas transmission line. The high pH of the water bleeding from the blister indicates that cathodic protection, which causes water to become alkaline or basic near cathodes, has been altering the environment beneath the disbonded coating. The gray surface beneath the blister has been exposed in Figure 8.65 and is not corroded.



**Figure 8.65** Underlying metal after non-adherent coating removed in the vicinity of the coating blister shown in Figure 8.64. Photo courtesy of R. Norsworthy, Polyguard Products, Inc.

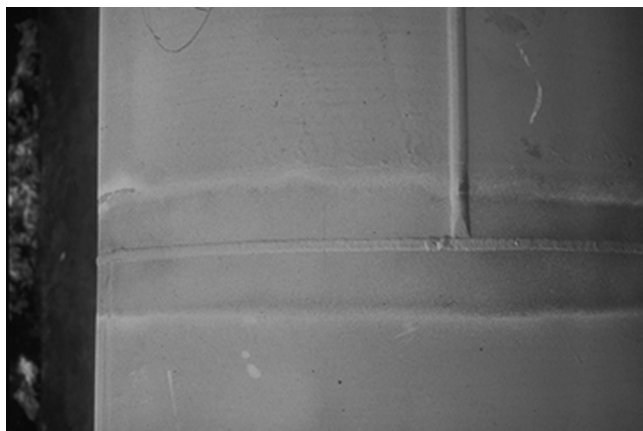


**Figure 8.66** Application of a field-applied coating at a girth weld on a pipeline. Photo courtesy of NACE International.

One of the problems with hard, damage-resistant coatings is that coating holidays, whether due to application problems or due to mechanical damage in shipping and construction, are hard to repair. The same properties that make holidays hard to repair also mean that field joint coatings, where coatings must be applied to the metal surface and to the adjacent pipeline coating, are also difficult.

Girth (circumferential) welds in pipelines must be coated in the field. This presents difficulties associated with surface preparation and coating application. Figure 8.66 shows the application of a field-applied coating system to a girth weld on a pipeline. Figure 8.67 shows





**Figure 8.67** Field joint after blast cleaning. The factory-applied coating has been ground to provide a gradual transition for the subsequent field-applied coating. Photo courtesy of NACE International.



**Figure 8.68** Wrinkled shrink sleeve due to soil loading.<sup>144</sup> Photo of courtesy of NACE International.

a girth-weld field joint after surface preparation and prior to coating application. The edges of the factory-applied coating have been ground smooth to allow for an easy transition from coating the bare metal surface to coating over the factory-applied coating.

The difficulty of applying coatings in the field led to the development and marketing of a variety of shrink-sleeve coatings for pipeline use. These coatings or wraps are applied as flexible solids to the pipeline exterior. Heat is applied to the sleeves, and this causes them to shrink and comply with the underlying surface profile. Properly applied shrink sleeves should be water tight and prevent corrosion of the underlying metal. Unfortunately, disbonded shrink sleeves shield underlying surfaces from cathodic protection. The pitting corrosion in Figure 5.25 was caused by dielectric shielding from a non-adherent shrink sleeve similar to the wrinkled shrink sleeve shown in Figure 8.68. Proponents of shrink sleeves claim that most cases of corrosion beneath non-adherent sleeves were caused by poor surface preparation prior to application of the shrink sleeves. Improvements in shrink-sleeve application methods have been reported.<sup>145,146</sup>

Most problems with external corrosion of pipelines are due to coatings problems. Cathodic protection is intended to supplement protective coatings, and it is effective when dielectric shielding is absent.<sup>146</sup>

### Internal Corrosion

The Carlsbad, New Mexico, pipeline incident in 2000 prompted increased attention on internal corrosion of pipelines. Internal pipeline coatings are seldom used,

because they are hard to apply at field joints, they can debond due to decompression, and they are subject to mechanical damage from inspection pigs and other sources.

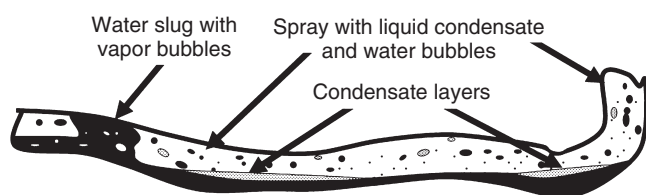
Oil pipelines have relatively few corrosion problems, because corrosive water can be entrained in oil–water emulsions and oil-wetted surfaces are not corroded. This approach does not work with low flow rates or in other circumstances where water can accumulate. Wicks and Fraser developed a model to explain when oil–water separation was likely to occur, and other models have been developed in recent years.<sup>26,47,147–149</sup> Water separation and corrosion at the bottom, 6 o'clock position has been reported in crude oil pipelines having as low as 0.5–2% water, depending on oil viscosity, flow rates, pipe diameters, and so on.<sup>150</sup>

Water separation, sludge accumulations, and paraffin deposits that cause corrosion are most likely to occur in locations with low flow rates, water separation from hydrocarbons, and solids accumulation.<sup>151</sup> Sludge and paraffin deposits are shown on the corrosion monitoring probes removed from a crude oil pipeline shown in Figure 8.69.<sup>150</sup> The 2006 Prudhoe Bay pipeline leaks have been reported to be caused by accumulated corrosion products and biofilms at the bottom of a crude oil pipeline. These leaks, and others, illustrate the need for internal cleaning and inspection operations using specialized pigs.

Gas pipelines are generally more corrosive than oil pipelines. This is primarily due to condensation of organic acids which cause any water in the pipeline to become corrosive. Figure 8.70 shows multiple phases forming in a gas pipeline. The water slug contains most



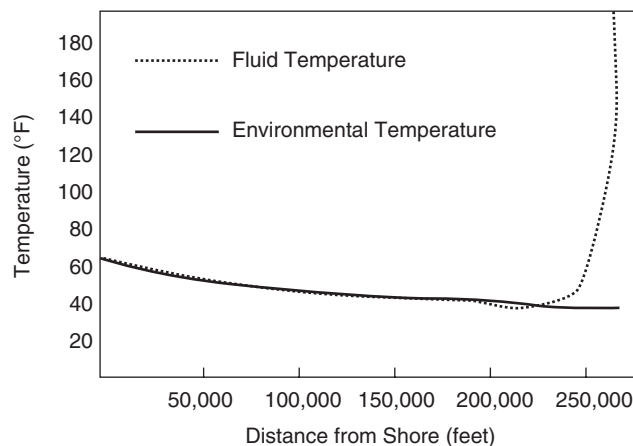
**Figure 8.69** Galvanic corrosion monitoring probe removed from a crude oil pipeline. Note the paraffin and sludge deposits.<sup>151</sup> Photo courtesy of NACE International, reproduced with permission.



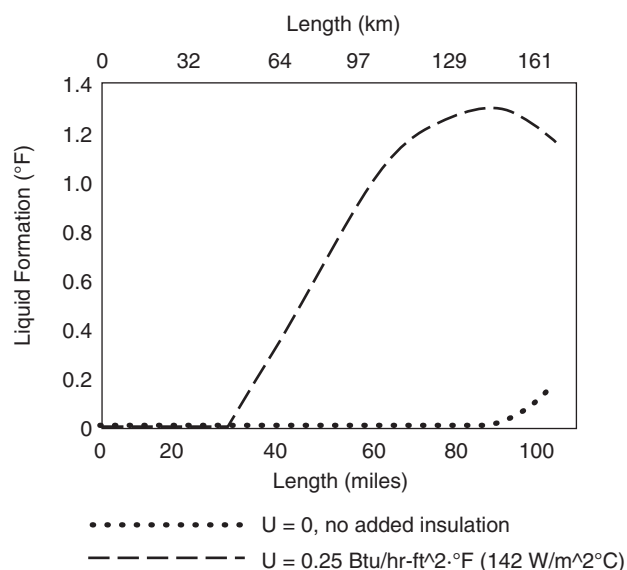
**Figure 8.70** Slugging and fluid flow through a multiphase piping system.

of the corrosion inhibitor, but condensed liquids containing organic acids and newly condensed, inhibitor-free water may collect on the top of the pipeline and cause corrosion. Corrosion inhibitors, dissolved in liquid water, may take up to a month to move through a pipeline, but condensation, which comes from the much faster-moving gas phase, can form at any time along the pipeline at any location where temperature and pressure considerations favor condensation. If the gas phase is not moving fast enough to cause droplets of corrosion-inhibitor-containing water from the bottom of the pipe to splash onto the upper portions of the pipe, then top-of-the-line corrosion can occur. Inhibitors should either be continuously injected into these pipelines or pigging operations, redistributing corrosion inhibitor from the bottom of the pipeline to the top, become necessary. Polymer spheres, gel pigs, and special corrosion-inhibitor spray pigs (Figure 6.60) are all used for this purpose.

Phase-separation prediction models are often used to suggest where corrosion is likely to occur.



**Figure 8.71** Pipeline fluid versus environmental temperatures for an offshore pipeline.



**Figure 8.72** Effect of thermal insulation on fluid temperatures in an onshore pipeline.

Figures 8.71 and 6.72 show the effects of distance from the source on fluid temperature for an offshore pipeline (Figure 8.71) and the effects of insulation on the fluid temperature of an onshore pipeline (Figure 8.72). The figures are simplified versions of the illustrations in the original reports.<sup>151,152</sup>

The results of fluid separation and temperature-pressure profile modeling are used to determine where corrosive conditions are most likely to occur. This information is used to determine where corrosion inhibitor injection points and corrosion monitoring probes should be located. They are also used to enable decisions on pigging schedules for corrosion inhibitor distribution,

internal pipeline cleaning, and inspection scheduling and methods.<sup>26,147–152</sup>

### Inspection and Condition Assessment

Pitting corrosion and environmental cracking are the most likely forms of degradation leading to pipeline failure. Unfortunately, the statistical distribution of pipeline pitting corrosion, which has been known and documented for decades, means that small corrosion probes or coupons are unlikely to identify the extent of corrosion-related wall loss.<sup>153</sup>

The common methods of pipeline inspection are:<sup>119</sup>

**Radiography**—normally used during construction, but also used during excavated inspections

**Ultrasound**—useful for wall thickness and hydrogen blistering inspections

**Magnetic Flux Leakage**—considered the “smartest” of pig-mounted inspection methods, although it may miss some cracking

**Visual Inspection**—requires excavation, but can identify important phenomena rapidly

Inspection pigs are routinely used for both internal and external corrosion condition surveys. These pigs, in addition to checking for corrosion phenomena, also identify buckling, denting, and other forms of mechanical anomalies. Unfortunately, not all pipelines and gathering lines are piggable. This is especially true at offshore risers, where the transitions from essentially horizontal piping to vertical piping make the systems most vulnerable to all forms of damage, both mechanical and chemical.

External corrosion survey methods have relied on cathodic protection surveys, but problems with dielectric shielding mean that some areas of serious corrosion have been missed by above-surface electrical surveys.<sup>145,146</sup>

All of these monitoring and inspection problems have led to the development of internal corrosion direct assessment (ICDA) and external corrosion direct assessment (ECDA) techniques and requirements.<sup>154</sup>

Table 8.22 lists NACE pipeline procedures and standards. The direct-assessment standards and techniques are new and subject to revision. Updated versions of these standards are likely to have significant changes as field experience provides input.

**TABLE 8.22 ECDA Data Elements<sup>a,154</sup>**

Data Elements	Indirect Inspection Tool Selection	ECDA Region Definition	Use and Interpretation of Results
<b>PIPE RELATED</b>			
Material (steel, cast iron, etc.) and grade	ECDA not appropriate for nonferrous materials. May reduce detection capability of indirect inspection tools.	Special considerations should be given to locations where dissimilar metals are joined.	Can create local corrosion cells when exposed to the environment.
Diameter			Influences CP current flow and interpretation of results.
Wall thickness			Affects critical defect size and remaining life predictions.
Year manufactured			Older pipe materials typically have lower toughness levels, which reduces critical defect size and remaining life predictions.
Seam type		Locations with pre-1970 low-frequency electric resistance welded (ERW) or flash-welded pipe with increased selective seam corrosion susceptibility may require separate ECDA regions.	Older pipe typically has lower weld seam toughness that reduces critical defect size. Pre-1970 ERW or flash-welded pipe seams may be subject to higher corrosion rates than the base metal.
Bare pipe	Limits ECDA application. Fewer available tools—See NACE SP0207 and NACE Standard TMD109.	Segments with bare pipe in coated pipelines should be in separate ECDA regions.	Specific ECDA methods provided in NACE SP0207 and NACE Standard TM0109.

TABLE 8.22 *Continued*

Data Elements	Indirect Inspection Tool Selection	ECDA Region Definition	Use and Interpretation of Results
<b>CONSTRUCTION RELATED</b>			
Year Installed			Affects time over which coating degradation may have occurred, defect population estimates, and corrosion rate estimates.
Route changes/modifications		Changes may require separate ECDA regions.	
Route maps/aerial photos		Provides general applicability information and ECDA region selection guidance.	Typically contain pipeline data that facilitate ECDA.
Construction practices		Construction practice differences may require separate ECDA regions.	May indicate locations at which construction problems may have occurred (e.g., backfill practices influence probability of coating damage during construction).
Locations of valves, clamps, supports, taps, mechanical couplings, expansion joints, cast iron components, tie-ins, insulating joints, etc.		Significant drains or changes in CP current should be considered separately; special considerations should be given to locations at which dissimilar metals are connected.	May affect local current flow and interpretation of results; dissimilar metals may create local corrosion cells at points of contact; coating degradation rates may be different from adjacent regions.
Locations of and construction methods used at casings	May preclude use of some indirect inspection tools.	Requires separate ECDA regions.	May require operator to extrapolate nearby results to inaccessible regions. Additional tools and other assessment activities may be required.
Locations of bends, including miter bends and wrinkle bends		Presence of miter bends and wrinkle bends may influence ECDA region selection.	Coating degradation rates may be different from adjacent regions; corrosion on miter and wrinkle bends can be localized, which affects local current flow and interpretation of results.
Depth of cover	Restricts the use of some indirect inspection techniques.	May require different ECDA regions for different ranges of depths of cover.	May affect current flow and interpretation of results.
Underwater sections and river crossings	Restricts the use of many indirect inspection techniques.	Requires separate ECDA regions.	Changes current flow and interpretation of results.
Locations of river weights and anchors	Reduces available indirect inspection tools.	May require separate ECDA regions.	Influences current flow and interpretation of results; corrosion near weights and anchors can be localized, which affects local current flow and interpretation of results.
Proximity to other pipelines, structures, high-voltage electric transmission lines, and rail crossings	May preclude use of some indirect inspection methods.	Regions where the CP currents are significantly affected by external sources should be treated as separate ECDA regions.	Influences local current flow and interpretation of results.



**TABLE 8.22** *Continued*

Data Elements	Indirect Inspection Tool Selection	ECDA Region Definition	Use and Interpretation of Results
<b>SOILS/ENVIRONMENTAL</b>			
Soil characteristics/ types (Refer to Appendixes A and C.)	Some soil characteristics reduce the accuracy of various indirect inspection techniques.	Influences where corrosion is most likely; significant differences generally require separate ECDA regions.	Can be useful in interpreting results. Influences corrosion rates and remaining life assessment.
Drainage		Influences where corrosion is most likely; significant differences may require separate ECDA regions.	Can be useful in interpreting results. Influences corrosion rates and remaining life assessment.
Topography	Conditions such as rocky areas can make indirect inspections difficult or impossible.		
Land use (current/ past)	Paved roads, etc., influence indirect inspection tool selection.	Can influence ECDA application and ECDA region selection.	
Frozen ground	May affect applicability and effectiveness of some ECDA methods.	Frozen areas should be considered separate ECDA regions.	Influences current flow and interpretation of results.
<b>CORROSION CONTROL</b>			
CP system type (anodes, rectifiers, and locations)	May affect ECDA tool selection.		Localized use of sacrificial anodes within impressed current systems may influence indirect inspection. Influences current flow and interpretation of results.
Stray current sources/ locations			Influences current flow and interpretation of results.
Test point locations (or pipe access points)		May provide input when defining ECDA regions.	
CP evaluation criteria			Used in postassessment analysis.
CP maintenance history		Coating condition indicator.	Can be useful in interpreting results.
Years without CP applied		May make ECDA more difficult to apply.	Negatively affects ability to estimate corrosion rates and make remaining life predictions.
Coating type (pipe)	ECDA may not be appropriate for disbanded coatings with high dielectric constants, which can cause shielding.		Coating type may influence time at which corrosion begins and estimates of corrosion rate based on measured wall loss.
Coating type (joints)	ECDA may not be appropriate for coatings that cause shielding.		Shielding caused by certain joint coatings may lead to requirements for other assessment activities.
Coating condition	ECDA may be difficult to apply with severely degraded coatings.		
Current demand			Increasing current demand may indicate areas where coating degradation is leading to more exposed pipe surface area.
CP survey data/history			Can be useful in interpreting results.

TABLE 8.22 Continued

Data Elements	Indirect Inspection Tool Selection	ECDA Region Definition	Use and Interpretation of Results
<b>OPERATIONAL DATA</b>			
Pipe operating temperature		Significant differences generally require separate ECDA regions.	Can locally influence coating degradation rates.
Operating stress levels and fluctuations			Affects critical defect size and remaining life predictions.
Monitoring programs (coupons, patrol, leak surveys, etc.)		May provide input when defining ECDA regions.	May affect repair, remediation, and replacement schedules.
Pipe inspection reports (excavation)		May provide input when defining ECDA regions.	
Repair history/records (steel/composite repair sleeves, repair locations, etc.)	May affect ECDA tool selection.	Prior repair methods, such as anode additions, can create a local difference that may influence ECDA region selection.	Provide useful data for postassessment analyses such as interpreting data near repairs.
Leak/rupture history (external corrosion)		Can indicate condition of existing pipe.	
Evidence of external MIC			MIC may accelerate external corrosion rates.
Type/frequency (third-party damage)			High third-party damage areas may have increased indirect inspection coating fault detects.
Data from previous over-the-ground or from-the-surface surveys			Essential for preassessment and ECDA region selection.
Hydrostatic testing dates/pressures			Influences inspection intervals.
Other prior integrity-related activities—CIS, ILI runs, etc.	May affect ECDA tool selection—isolated vs. larger corroded areas.		Useful postassessment data.

<sup>a</sup> Those items that are shaded are most important for tool selection purposes.

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